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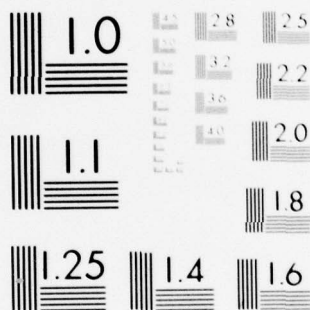
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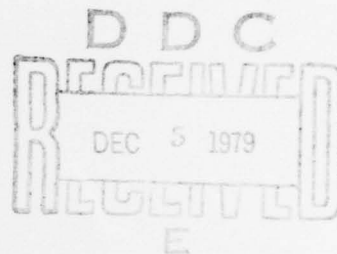
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INVESTIGATIONS OF THE SAFETY OF Li/SOCl₂ BATTERIES

AD A 077894

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Analysis of products from Li/SOCl_2 cells during various modes of operation was carried out using cyclic voltammetry and infrared spectro- metry. Infrared spectral data indicated that LiAlSCL_2 and probably LiAlS_2 are formed in cathode limited Li/SOCl_2 cells during forced overdischarge and resistive load overdischarge. These compounds are formed from the		

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reaction of Li_2S , produced in the cell under these operational modes, with LiAlCl_4 . It has been found that the lithium thioaluminum compounds can be prepared from the reaction between Li_2S and AlCl_3 .

Analysis of products from cells utilizing $\text{Li}_2\text{O}/\text{AlCl}_3$ based electrolytes did not show any significantly different products after overdischarge or constant current "charge".

Preliminary studies showed that $\text{Li}_2\text{S}/\text{AlCl}_3$ based electrolytes may be useful as alternatives to LiAlCl_4 in Li/SOCl_2 batteries.

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I. INTRODUCTION

In recent years there has been considerable research and development on ambient temperature, high energy density Li cells. A particularly promising system is based on SOCl_2 (1,2). Here, SOCl_2 serves as both a solvent and depolarizer for the cell. These cells have delivered 100 Whr/lb and 40 W/lb at the 2.5-hour rate and, as usual, higher energy densities at lower discharge rates (3). According to one report (4) they can deliver as much as 300 Whr/lb at low rates. Clearly this is a very promising system with many applications where high energy density and high rate are required.

The cell has two problems: (1) under a variety of circumstances, the cell has shown a tendency to explode, (2) after high temperature storage, it shows voltage delay.

The objective of this program is to explore the causes and find solutions to the explosion hazards in the Li/ SOCl_2 cells. Three types of explosion have been reported: (1) cells explode on short circuit; (2) cells explode on forced overdischarge; (3) cells explode on resistive load overdischarge. Clearly, any high rate, high energy density system such as Li/ SOCl_2 has the possibility of a thermal runaway type of explosion. It is not surprising that a hermetically sealed D-cell, which can deliver in excess of 20 amps, might explode when short circuited -- it just is not possible to remove the waste heat. However, this problem appears to have been solved with low pressure vents (100-300 psi) and with appropriate fuses incorporated into the cell (5,6).

The other two types of explosion are of greater concern. The forced overdischarge situation may be experienced by a cell in a battery package. Explosion on resistive load overdischarge implies that any completely discharged cell still connected to a piece of equipment is a hazard. No clear documentation of the explosion hazard on resistive load overdischarge is found in the literature. Forced overdischarge explosions have been documented for D-size (5) and C-size (7,8) Li/ SOCl_2 cells. This type of explosion, occurring after cell-voltage reversal, takes place without prior temperature or pressure rise and appears to be chemical in its origin. Our experiments suggests that forced overdischarge explosions would occur only in anode limited cells (7,8). Individual electrode potential measurements during discharge and overdischarge showed that the anode was at $\geq 4.0\text{V}$ for a considerable length of time prior to an explosion. The nature of the explosions suggests that they are caused by sensitive chemicals generated in oxidation reactions of SOCl_2 or other materials present in the cell.

In the present program, we have been engaged in analytical studies aimed at characterizing the various materials under forced overdischarge conditions. The principal analytical techniques have been cyclic voltammetry and IR spectrometry. During the present quarter, these studies have continued.

Major developments have been (i) identification of several reaction products from cathode limited cells after forced overdischarge and (ii) discovery of a new supporting electrolyte based on $\text{Li}_2\text{S}/\text{AlCl}_3$ for Li inorganic electrolyte cells.

Attempts to fully characterize the various substances generated in anode limited cells during forced overdischarge continued. We have also investigated the behavior of Li/SOCl_2 cells during resistive load overdischarge. Several materials formed during this mode of operation have been characterized.

II. PRODUCT ANALYSIS FROM Li/SOCl₂ CELLS

Analytical work on product characterization from Li/SOCl₂ cells after discharge, overdischarge and constant current "charge" has continued. The analytical techniques have been IR spectrometry and in situ cyclic voltammetry as described in the second quarterly report. All the cells for these studies were of the prismatic type and tested in a slightly flooded configuration. The larger amounts of electrolyte were needed to have solution left for analysis after the galvanostatic experiments. The cell set up for in situ cyclic voltammetry has also been described in the second quarterly report. The construction parameters for the cells are shown in Table 1. The extent of discharge and overdischarge for each cell before the analytical test are shown in Table 2.

1. Products from Forced Overdischarged Cathode Limited Cells

The IR spectrum of the electrolyte from a typical cathode limited cell (P-36) after forced overdischarge is shown in Fig. 1. The discharge and overdischarge for the cell are shown in Fig. 2. The cell, discharged at 36 mA had a capacity to zero volt of 1.21 Ah and the IR spectrum was obtained after 1.08 Ah of overdischarge. The spectrum shows the SO₂ peaks at 1340 cm⁻¹ and 1155 cm⁻¹. A weak shoulder is present at 1065 cm⁻¹ and this peak coincides with the first overtone band of the S-Cl stretch in S₂Cl₂ near 550 cm⁻¹. Since the S-Cl stretching absorptions in SOCl₂, and the Al-Cl stretching absorptions in AlCl₃ all occur in the region 500-550 cm⁻¹, it cannot be established unequivocally whether S₂Cl₂ is present in the electrolyte.

The IR spectrum also shows two strong absorptions at 790 cm⁻¹ and 665 cm⁻¹. These peaks have been found in the electrolyte from all cathode limited cells after forced overdischarge. In the electrolyte from cathode limited cells, terminated just at the end of discharge or overdischarged very little, say 50 mAh, these peaks were not present or sometimes present as weak bands.

In order to identify these peaks, IR spectra of solutions of various materials in SOCl₂ were obtained. From these experiments it was found that these peaks were associated with a product of reaction between Li₂S and LiAlCl₄. When Li₂S (anhydrous, Foote Mineral Co.) was added to SOCl₂ at room temperature there was no apparent solubility nor was there any apparent reaction between the two materials. On the other hand when anhydrous Li₂S is added to SOCl₂/LiAlCl₄ electrolyte an exothermic reaction ensues with the formation of a white precipitate. The IR spectrum of the solution product from a reaction between

Table 1

Cell Parameters for Prismatic Li/SOCl₂ Cells

Cell No.	Cell Configuration	Carbon Electrode			Lithium Electrode		Electrolyte LiAlCl ₄ /SOCl ₂	
		Average Thickness (mm)	Total Area Facing Li (cm ²)	Approximate Amount of Carbon (mg)	Area (cm ²)	Amount (Ah)	Con. LiAlCl ₄ (M)	Vol. (ml)
36	Li/C/Li/C/LiC/Li (CL) ^a	0.62	36	360	36	2.01	1.8	4
37	CL	0.61	36	340	36	2.01	1.8	4
41	C/Li/C/Li/C (AL) ^b	0.63	24	420	24	0.63	1.0 ^e	4
42	CL	0.62	36	360	36	2.01	1.0 ^c	4
43	CL	0.62	36	375	36	2.01	1.0 ^d	4
44	AL	0.63	24	380	24	0.63	1.8	4
46	AL	0.62	24	385	24	0.63	1.0 ^c	4
47	CL	0.62	36	340	36	2.01	1.8 ^e	4
48	AL	0.62	24	336	24	0.63	1.8 ^d	4
								141Ω Load
								24
								36
								36 ^e

^aCL → cathode limited.^bAL → anode limited.^cLi₂O/AlCl₃ electrolyte, 1M Li⁺.^dSO₂Cl₂/1.8M LiAlCl₄.^eThe cell was "charged".

Table 2
Analytical Test Summary of Prismatic Li/SOCl₂ Cells

Cell No.	Cell Capacity (mAh)	Test Performed After			
		Discharge, mAh		Overdischarge, mAh	
		IR	CV	IR	CV
36	1210	-	-	1080	1080
37	~1100	-	-	17 hr thru 99 Ω	17 hr thru 99 Ω
41	560	-	-	304	304
42	1210	-	-	950	950
43	a	-	-	1530 ^a	1530 ^a
44	~500	-	-	20 hr thru 141 Ω	20 hr thru 141 Ω
46	b	-	-	1580	1580
47	a	-	-	3350 ^a	3350 ^a
48	b	-	-	3250	3250

^aThe cell was charged.

^bCell without Li.

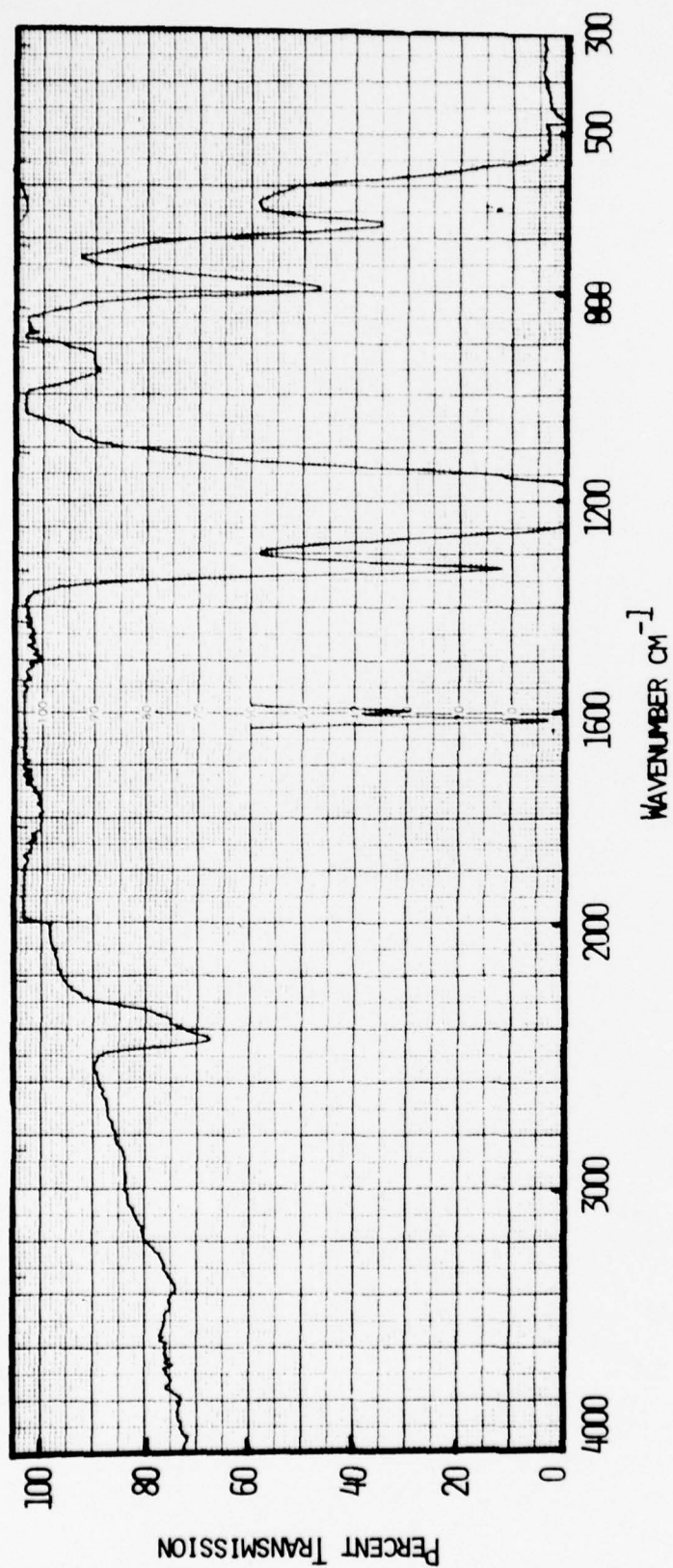


Fig. 1. Infrared spectrum of electrolyte from Li/SOCl₂ cell P-36 after forced overdischarge shown in Fig. 1.

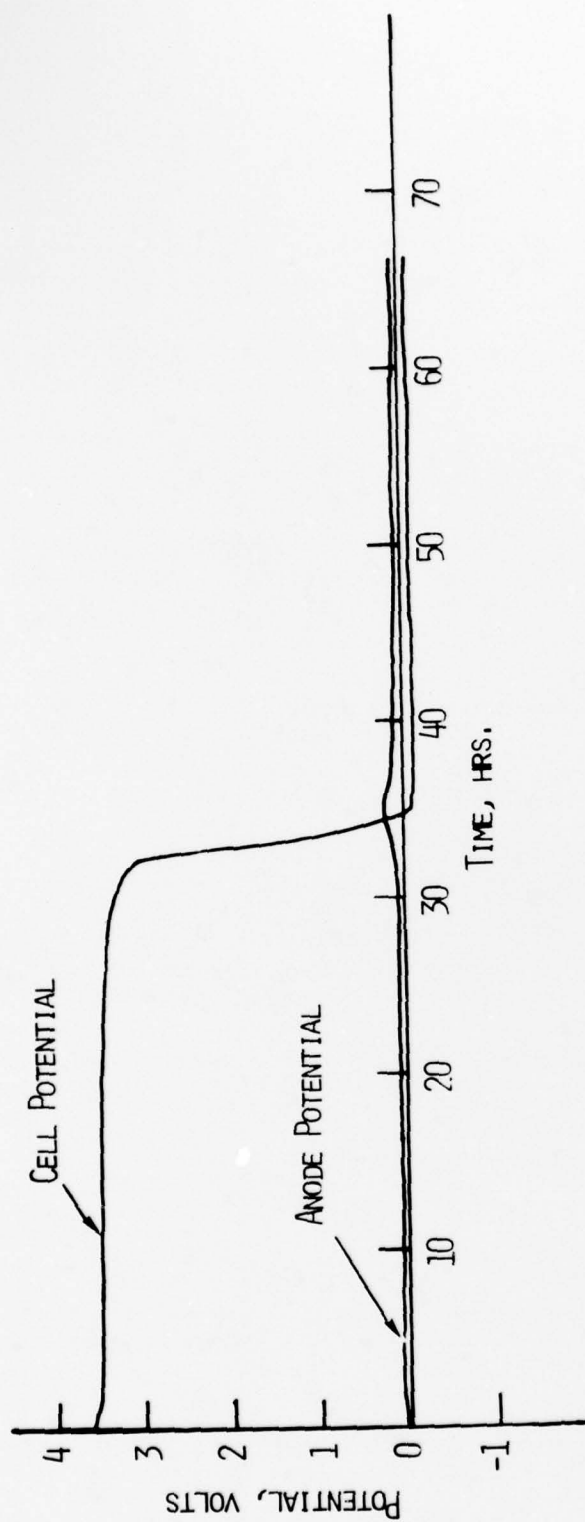
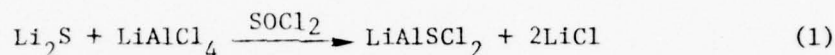


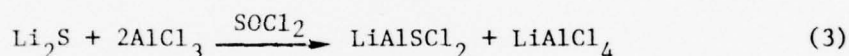
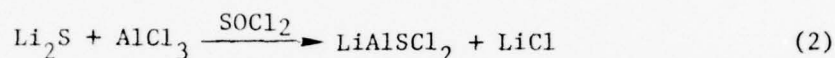
Fig. 2. Discharge and overdischarge curves for Li/SOCl₂ cell P-36. Current = 36 mA.

Li_2S and LiAlCl_4 , treated in 1:1 molar ratio in SOCl_2 is shown in Fig. 3. The spectrum also shows the two peaks at 790 cm^{-1} and 665 cm^{-1} with relative intensities essentially identical to those in Fig. 1.

It appears that Li_2S reacts with LiAlCl_4 as shown in Equation 1 to form LiAlSCl_2 and LiCl of which the former is soluble in SOCl_2 .

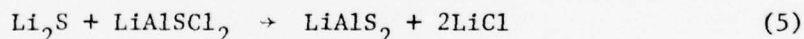
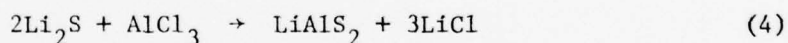


In the IR spectrum, the peaks at 790 cm^{-1} and 665 cm^{-1} are most probably due to Al-S stretch and Al-Cl stretch respectively of LiAlSCl_2 . We have found that LiAlSCl_2 can also be prepared by the reaction of Li_2S and AlCl_3 in SOCl_2 * according to the reactions 2 and 3.



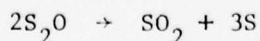
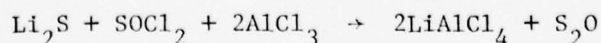
The IR spectra of the solutions from reactions 2 and 3 are shown in Figs. 4 and 5. They have features essentially identical to those in Fig. 3. We have also found that solutions of LiAlSCl_2 in SOCl_2 have conductivities similar to that of LiAlCl_4 and that LiAlSCl_2 can be an alternative electrolyte for Li/SOCl_2 cells. These aspects of LiAlSCl_2 will be discussed in the next section.

When Li_2S and AlCl_3 are mixed in a 2:1 molar ratio in SOCl_2 or when Li_2S is added to $\text{LiAlSCl}_2/\text{SOCl}_2$ solutions, the following reactions seem to take place.



LiAlS_2 is apparently insoluble or has very little solubility in SOCl_2 and it precipitates out as a dark material along with LiCl . In the IR spectra of these solutions the two absorptions at 790 cm^{-1} and 665 cm^{-1} are present as very weak bands.

*In these solutions we have not ruled out the possibility of parallel reactions such as,



There is no reaction between Li_2S and SOCl_2 at room temperature.

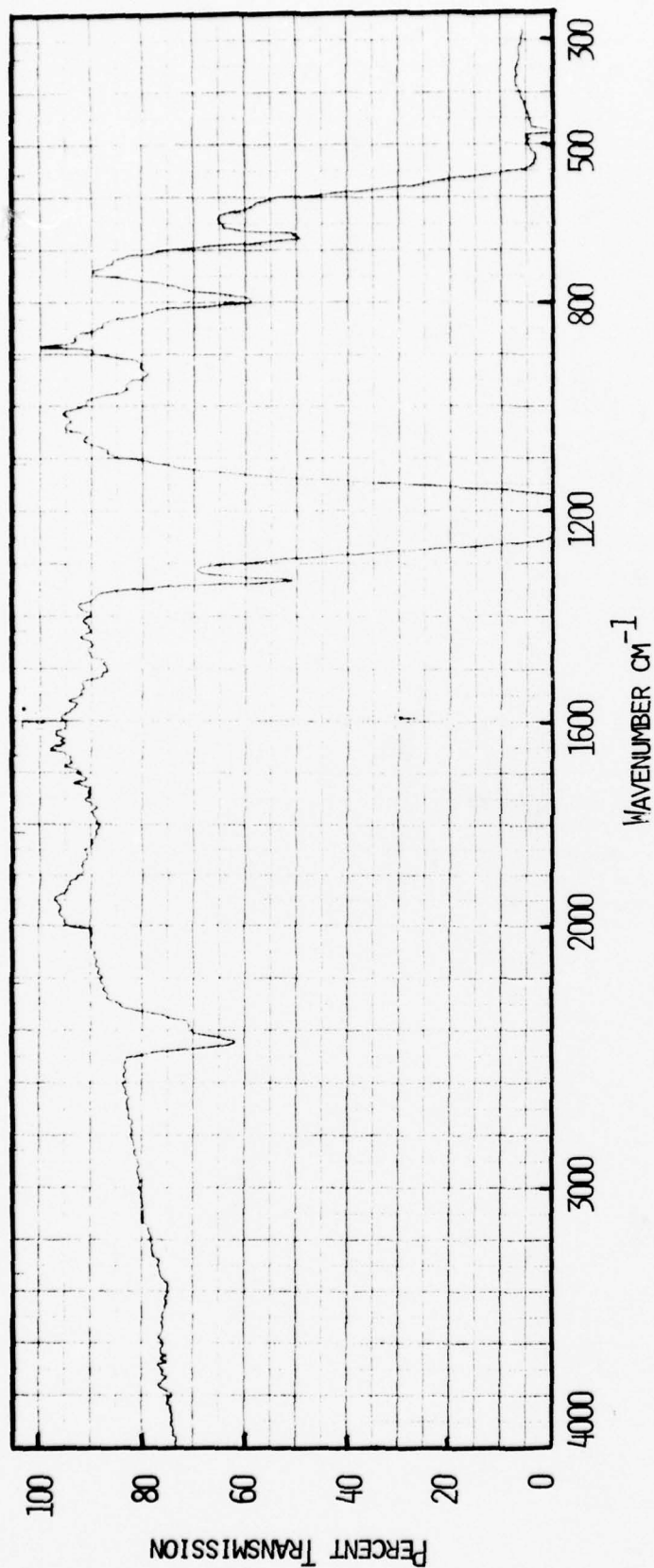


Fig. 3. Infrared spectrum of the solution product from the reaction of equimolar amounts of Li_2S and LiAlCl_4 in SOCl_2 .

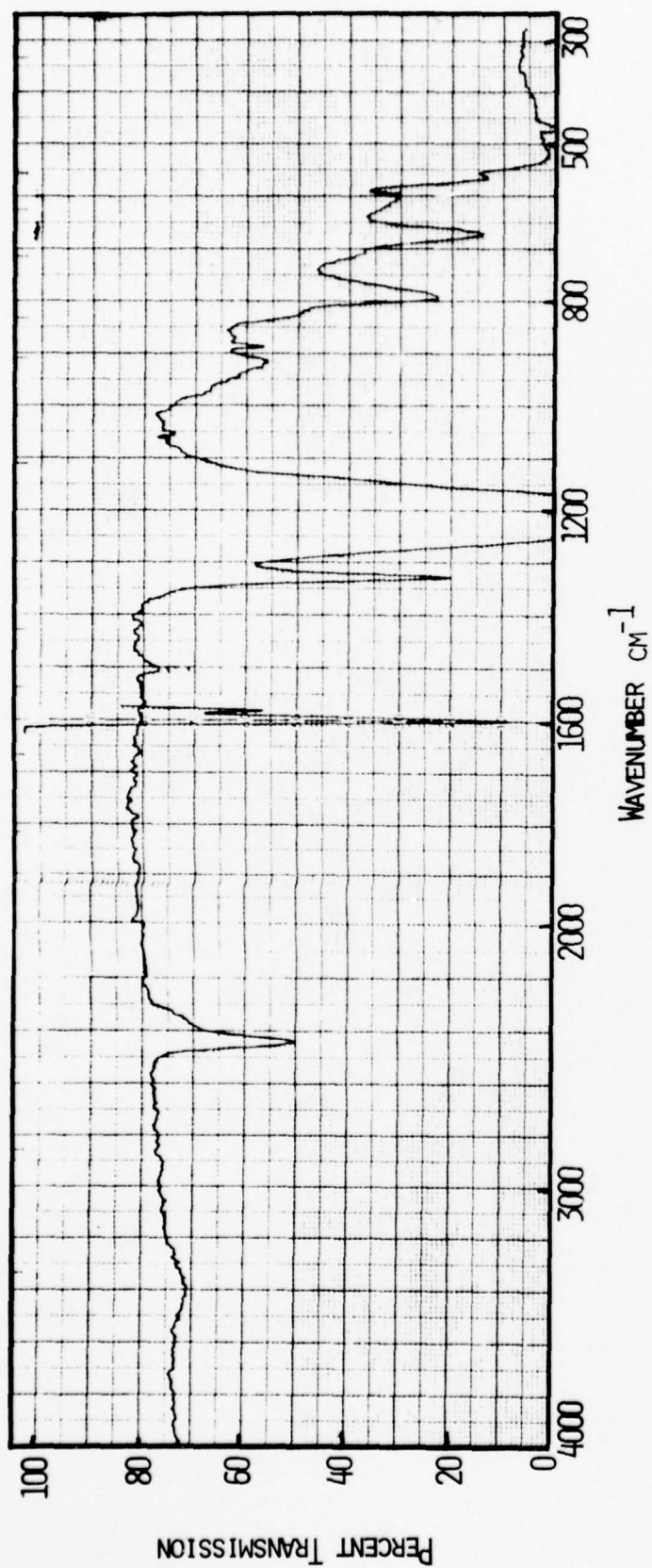


Fig. 4. Infrared spectrum of the solution product from reaction between equimolar amounts of Li_2S and AlCl_3 in SOCl_2 .

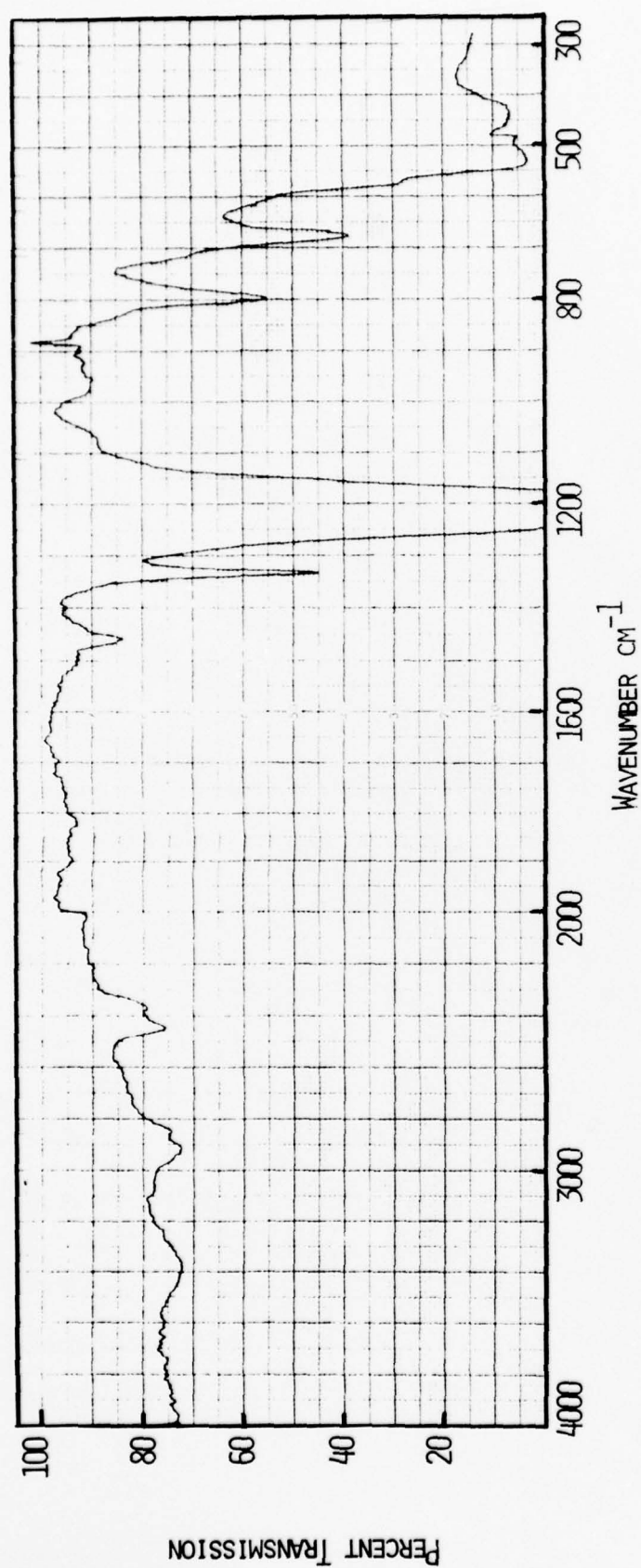
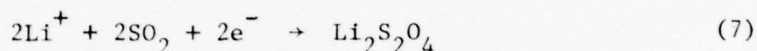


Fig. 5. Infrared spectrum of the solution product from the reaction of one mole of Li_2S with two moles of AlCl_3 in SOCl_2 .

The evidences presented here suggest that when cathode limited cells are forced overdischarged Li_2S is formed and that Li_2S reacts immediately with LiAlCl_4 to form LiAlSCl_2 and probably LiAlS_2 . As would be seen later, these aluminum-sulfur compounds are also formed in the electrolyte from resistively overdischarged cells. It seems that in discharged cells which invariably contains S as a discharge product, the formation of Li_2S is a spontaneous process, (Equation 6).

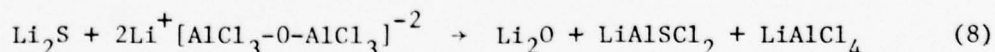


Since both S and SO_2 are discharge products of Li/SOCl_2 cells and have closely lying reduction potentials, it is logical to assume that SO_2 also can undergo reduction as shown in Equation 7, probably to form lithium dithionite, $\text{Li}_2\text{S}_2\text{O}_4$, Equation 7.



To date we do not have any evidence to confirm this. Qualitative tests for $\text{S}_2\text{O}_4^{2-}$ were negative. It is possible that $\text{Li}_2\text{S}_2\text{O}_4$, if formed, could react with LiAlCl_4 forming aluminum dithionite derivatives, which may be unstable and thereby escape qualitative test for $\text{S}_2\text{O}_4^{2-}$ species.

We have also analyzed the electrolyte from forced overdischarged, cathode limited cells which contained $\text{Li}_2\text{O}/\text{AlCl}_3$ based supporting electrolyte (9). The discharge and overdischarge curves for cell P-42 with $0.5\text{M Li}_2\text{O}/1.0\text{M AlCl}_3/\text{SOCl}_2$ is shown in Fig. 6. The cell capacity of 1.21 Ah to zero volt is virtually identical to that found in similar cells with $\text{SOCl}_2/\text{LiAlCl}_4$ electrolyte. The IR spectrum of the electrolyte from cell P-42 was obtained after 0.95 Ah of overdischarge and is shown in Fig. 7. The spectrum also shows the peaks at 790 cm^{-1} and 665 cm^{-1} but at much lower intensities than in the electrolyte from the cell containing LiAlCl_4 for the same extent of overdischarge. The actual supporting electrolyte in these solutions according to Gabano et al., is $2\text{Li}^+[\text{AlCl}_3\text{-O-AlCl}_3]^{-2}$. The reaction of Li_2S to form LiAlSCl_2 could then be as shown in Equation 8. The actual concentration of Al species in these electrolytes is only 1M instead of the 1.8M in our



normal electrolyte. Out of this only half the amount of AlCl_3 is converted to LiAlSCl_2 according to Equation 8. Thus the lower amount of LiAlSCl_2 observed in cell P-42 could result from a concentration effect of the Al species. That is, all of the Li_2S formed in the cell may not have been converted to LiAlSCl_2 .

2. Products from Cathode Limited Cells after Resistive-Load Overdischarge

The discharge and overdischarge behavior of a typical cathode limited cell, P-37, on resistive load is shown in Fig. 8. The cell was discharged

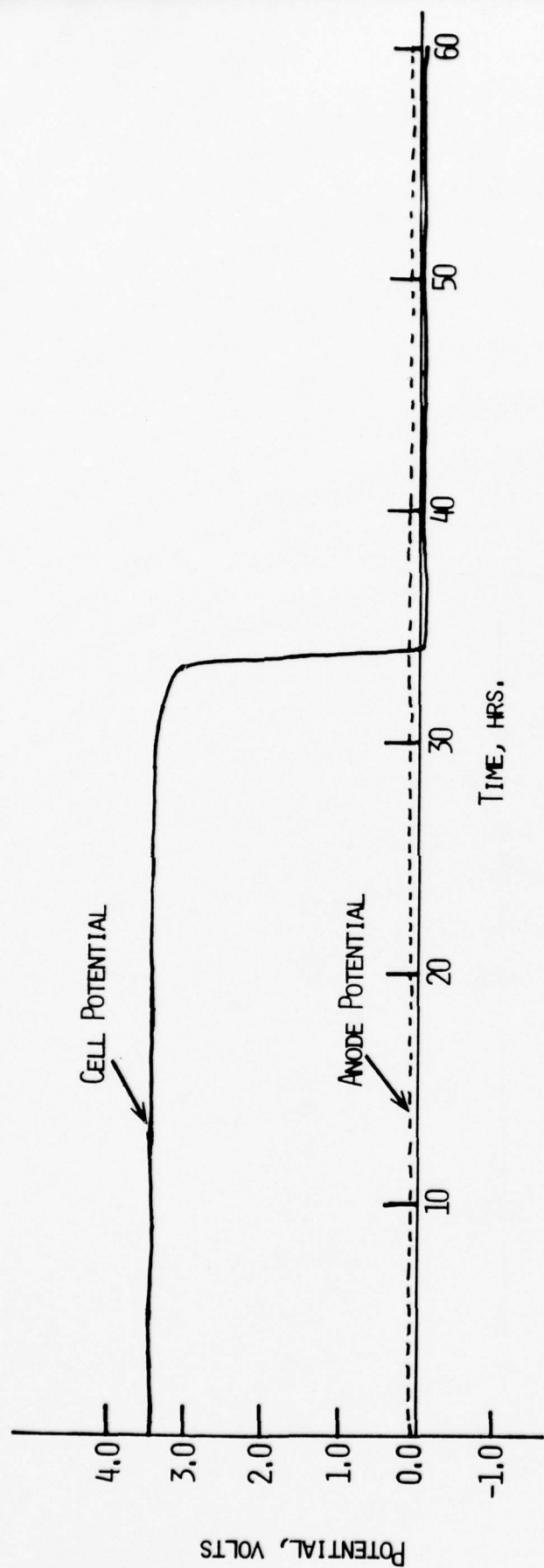


Fig. 6. Galvanostatic discharge curve for cathode limited cell P-42.
Current = 36 mA.

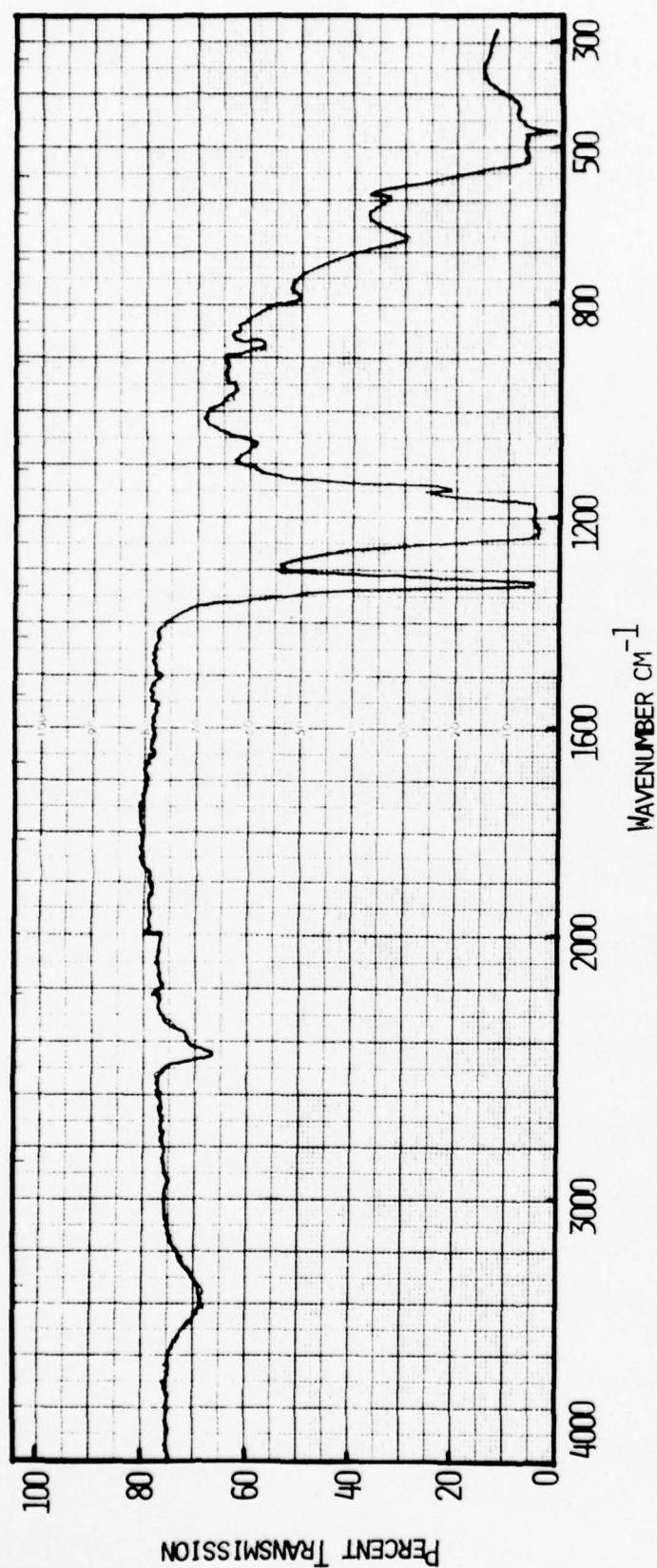


Fig. 7. Infrared spectrum of the electrolyte from cell P-42 after the overdischarge shown in Fig. 6.

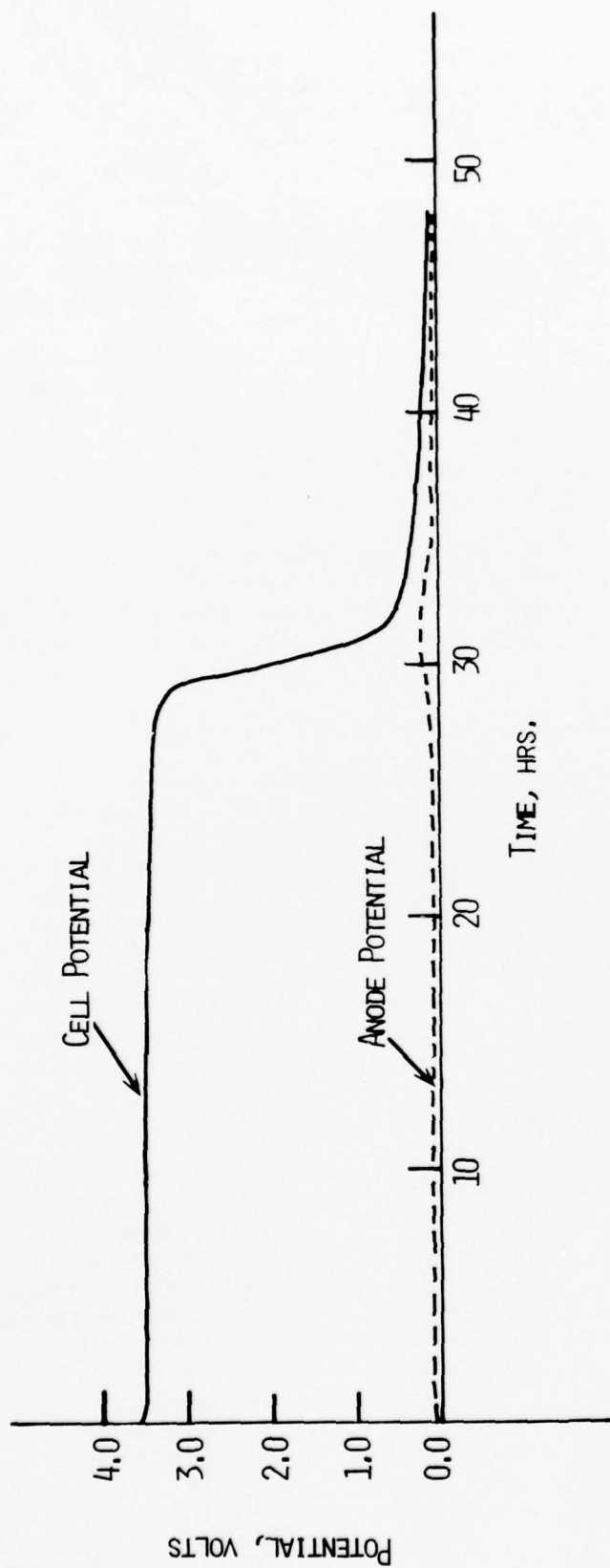


Fig. 8. Discharge of cathode limited cell P-37 through 99Ω load.

through 99 Ω load so that the initial current drainage was 35 mA. The cell had a capacity of ~ 1.2 Ah, corresponding to 3.23 Ah/g carbon utilization. The cell was allowed to overdischarge (< 0.5 V) for 17 hours through the 99 Ω load before electrolyte was analyzed by cyclic voltammetry and IR spectrometry. The infrared spectrum is shown in Fig. 9. The spectrum is quite similar to that of the electrolyte from the forced overdischarged cathode limited cells. The two absorptions at 790 cm^{-1} and 665 cm^{-1} indicate that LiAlSCl_2 is produced under resistive load overdischarge also. It seems that when S is present in these cells, the formation of Li_2S occurs spontaneously if the potentials are favorable, i.e., below ~ 2.3 volt, the reduction potential of S.

The cyclic voltammogram of the electrolyte, recorded on a glassy carbon electrode just prior to the IR spectral measurement is shown in Fig. 10. The voltammogram shows that some Cl_2 may be present in solution. Previously, we have obtained similar voltammograms in electrolytes from forced overdischarged cathode limited cells.

3. Products from Anode Limited Cells after Resistive-Load Overdischarge

The discharge and overdischarge behavior for a typical anode limited cell, P-44, on resistive load is shown in Fig. 11. The cell was discharged through 141 Ω load, corresponding to an initial current drainage of 24 mA. Its capacity to zero volt was ~ 0.5 Ah. At the end of discharge the anode potential rises to positive values and during overdischarge remains steady at 3.6V. The cell potential remains steady at +100 mV. The electrolyte was analyzed after overdischarging the cell for 20 hour through 141 Ω . The IR spectrum is shown in Fig. 12. This spectrum also shows the peaks at 790 cm^{-1} and 655 cm^{-1} indicating that LiAlSCl_2 is present in solution. This result is somewhat surprising since the potential regions do not appear to be favorable for Li_2S formation. We are further investigating the products from these types of cell.

4. Products from Anode Limited Cells after Forced Overdischarge

In the second quarterly report we have discussed the results of IR spectral and in situ cyclic voltammetry studies carried out to characterize products from forced overdischarged anode limited Li/SOCl_2 cells. The products identified were Cl_2 and a material exhibiting IR absorption at 1070 cm^{-1} . We have also shown that the compounds, SO_2Cl_2 , SCl_2 and $\text{SOCl}^+\text{AlCl}_4^-$ are also formed in these cells under oxidizing environments at varying test conditions such as discharge of cells without Li on the anode and constant current change. Our phenomenological studies had revealed that anode limited cells exploded on occasions during forced overdischarge. The nature of the phenomenon suggested that they were caused by detonation of energetic substances accumulated in the cell, probably by oxidation reactions. The possibility that the energetic substance is an intermediate which accumulates only under spectral circumstances has been investigated in these cells by cyclic voltammetry studies of $\text{SOCl}_2/\text{LiAlCl}_4$.

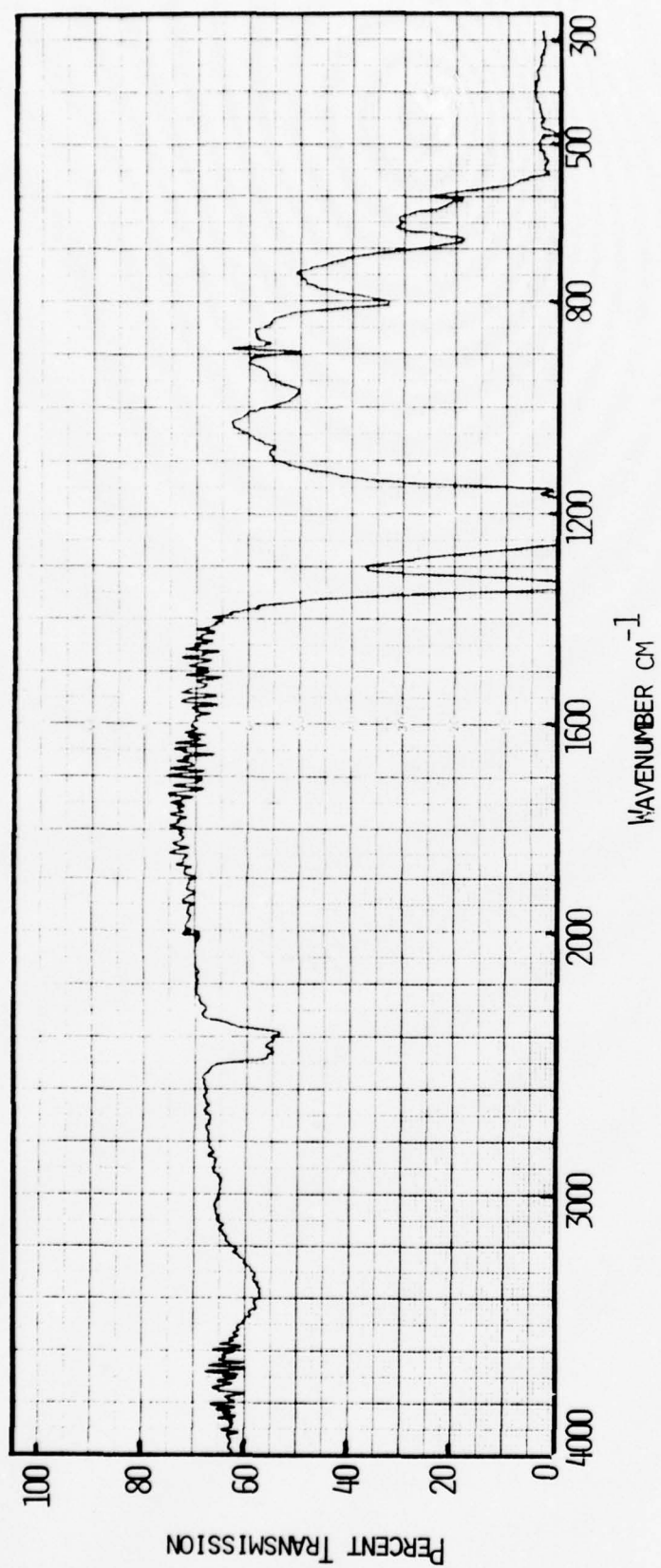


Fig. 9. Infrared spectrum of the electrolyte from cell P-37 after the test shown in Fig. 8.

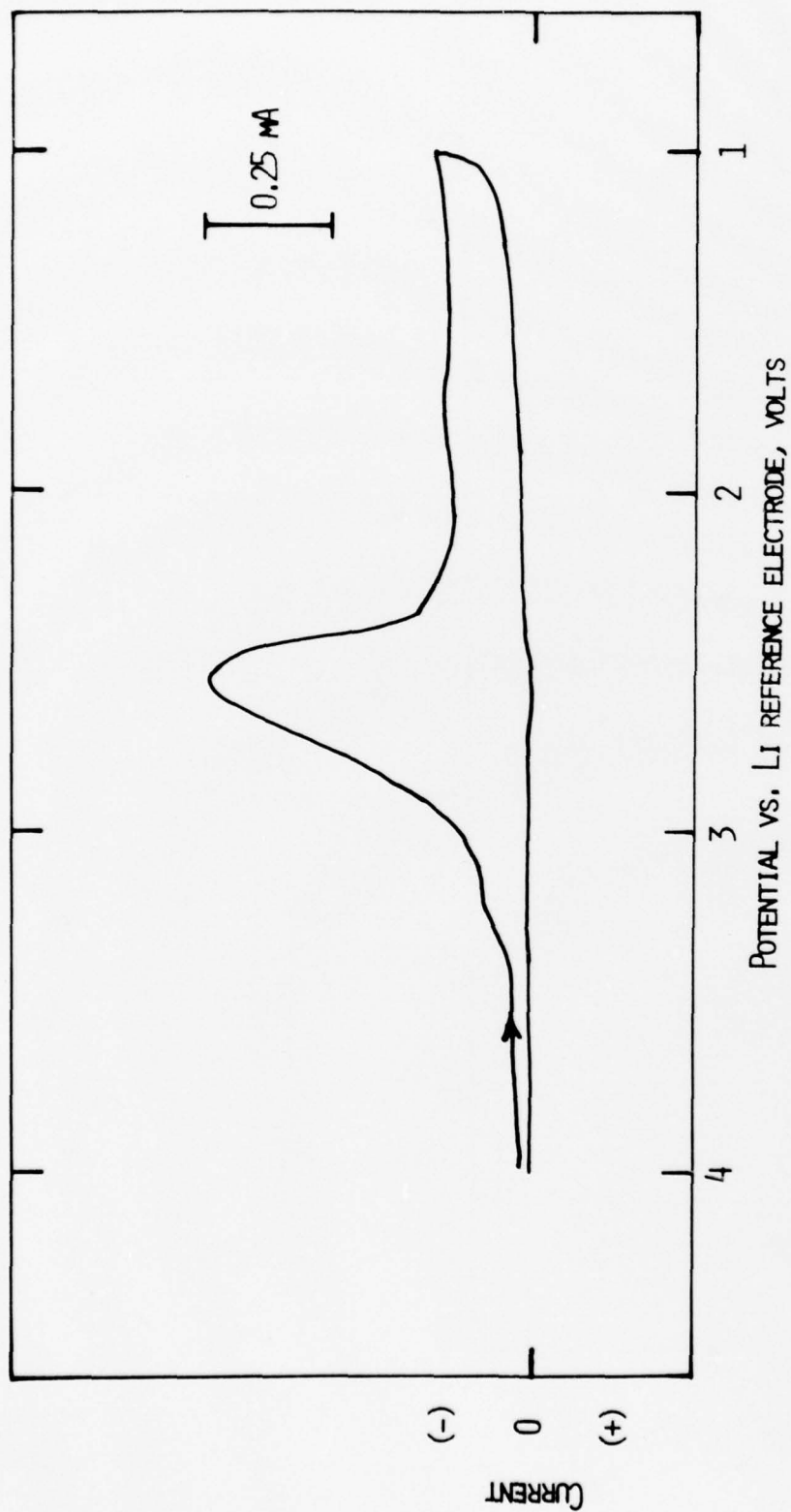


Fig. 10. Cyclic voltammogram of the electrolyte from cell P-37 after the overdischarge shown in Fig. 8. Sweep rate = 200 mV/sec. Cathodic scan first.

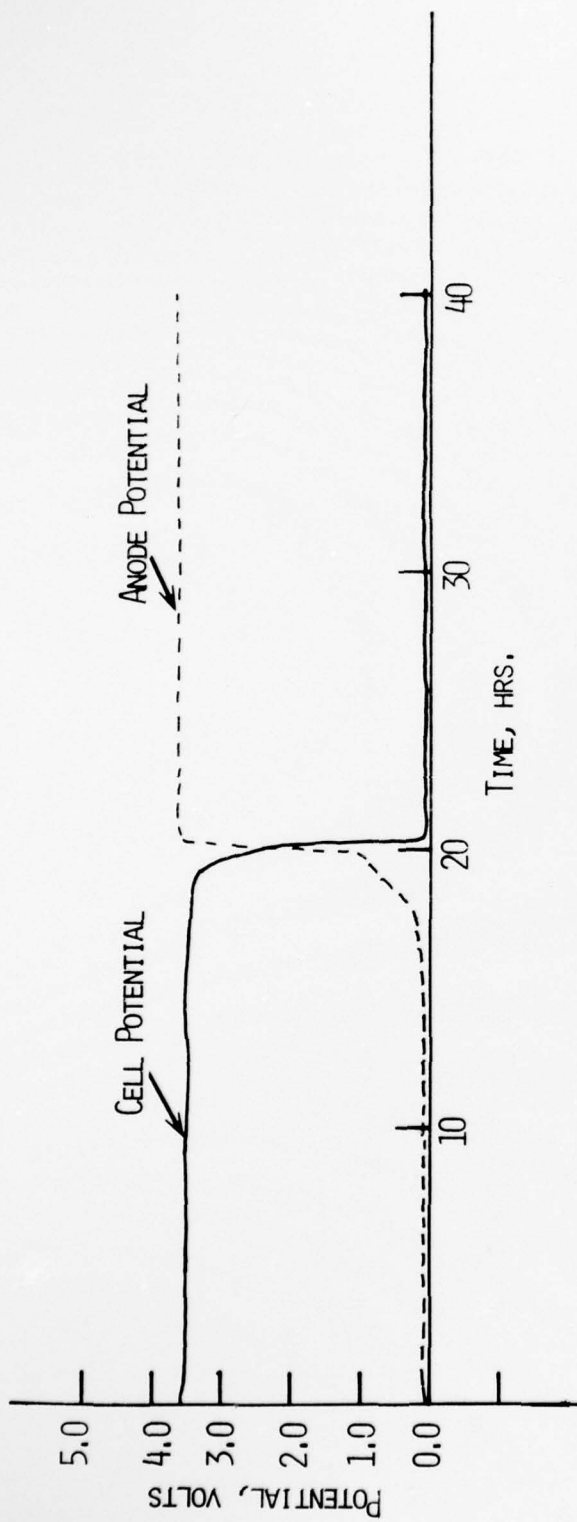


Fig. 11. Discharge of anode limited cell P-44 through 141Ω load.

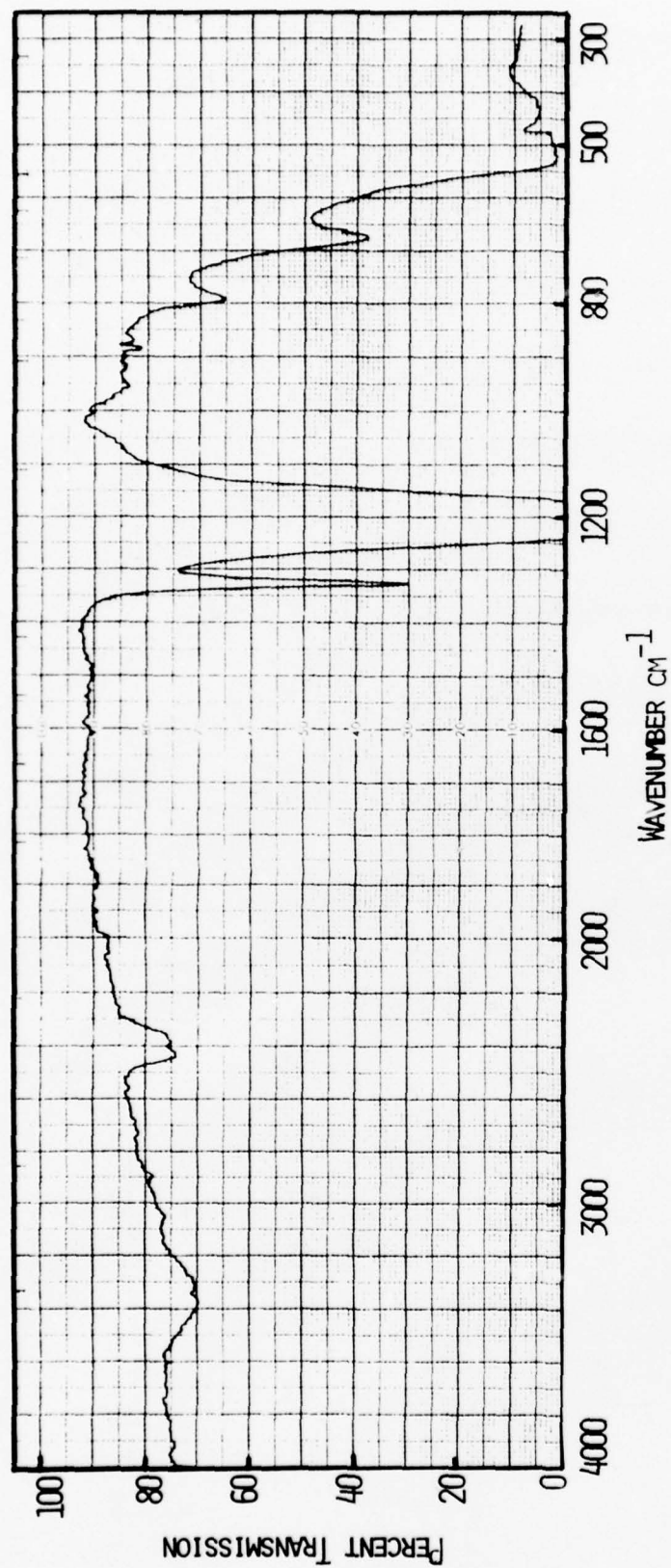


Fig. 12. Infrared spectrum of the electrolyte from cell P-44 shown in Fig. 11.

solutions with various additives. The materials identified so far do not appear to be explosive. Nevertheless, we have yet to identify the substance with the 1070 cm^{-1} absorption in the IR spectrum.

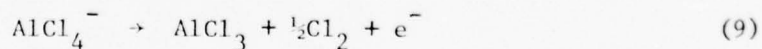
Much of the work therefore has been centered on characterizing this material as well as identifying the circumstances under which it is formed.

4.1 Role of Supporting Electrolyte

The possible role of the supporting electrolyte was investigated by studying the products from cells utilizing the $\text{Li}_2\text{O}/\text{AlCl}_3$ based electrolyte (9). The electrolyte containing 1M Li^+ ions was prepared by stirring Li_2O and AlCl_3 in a 1:2 molar ratio in SOCl_2 as described previously (9). The various small prismatic cells tested and their construction parameters are given in Table 1.

Cell P-41 was essentially identical to the anode limited cell P-18 containing $\text{SOCl}_2/1.8\text{M LiAlCl}_4$. Cell P-18 was discussed in the 2nd quarterly report. Cell P-41 was discharged and overdischarged at 24 mA (1 mA/cm^2 of Li electrode area), the same current density used in P-18. The discharge and overdischarge curves for cell P-41 are shown in Fig. 13. It yielded a capacity of 0.56 Ah . The IR spectrum of the electrolyte after 304 mAh of overdischarge is shown in Fig. 14. The cyclic voltammogram on glassy carbon electrode is shown in Fig. 15. The IR spectrum shows the presence of the material exhibiting the absorption at 1070 cm^{-1} . The cyclic voltammogram shows that Cl_2 is also present. It thus appears that the type of products and their relative amounts are essentially the same in both of the electrolytes under similar regimes of forced overdischarge.

Cell P-46 also contained $\text{Li}_2\text{O}/\text{AlCl}_3$ based electrolyte with 1M Li^+ ion concentration. But the cell was constructed without Li on the anode. Test results for similar cells have been discussed previously and the data are useful to elucidate the possible role of Li in the production or in the consumption of potentially explosive materials. Cells without Li represents an extreme case of anode limited configuration. The discharge curve for cell P-46 at a current of 24 mA is shown in Fig. 16. The electrolyte was analyzed after 1.58 Ah of discharge. The IR spectrum, shown in Fig. 17 reveals that SO_2 and the material exhibiting the absorption at 1070 cm^{-1} are present. In the electrolyte from similar cells tested previously with $\text{SOCl}_2/\text{LiAlCl}_4$, IR spectrum showed $\text{SOCl}^+\text{AlCl}_4^-$ also. In these cells the complex, $\text{SOCl}^+\text{AlCl}_4^-$, might have formed via the reactions



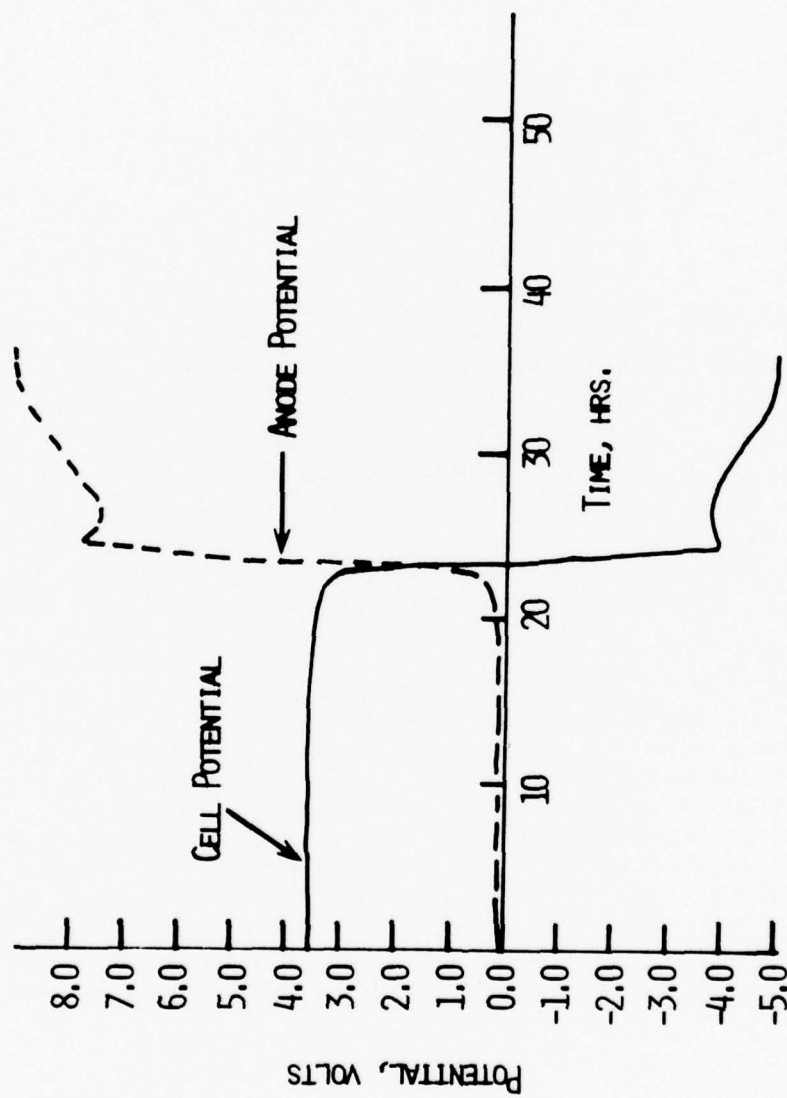


Fig. 13. Discharge and overdischarge curves for cell P-41. Current = 24 mA.

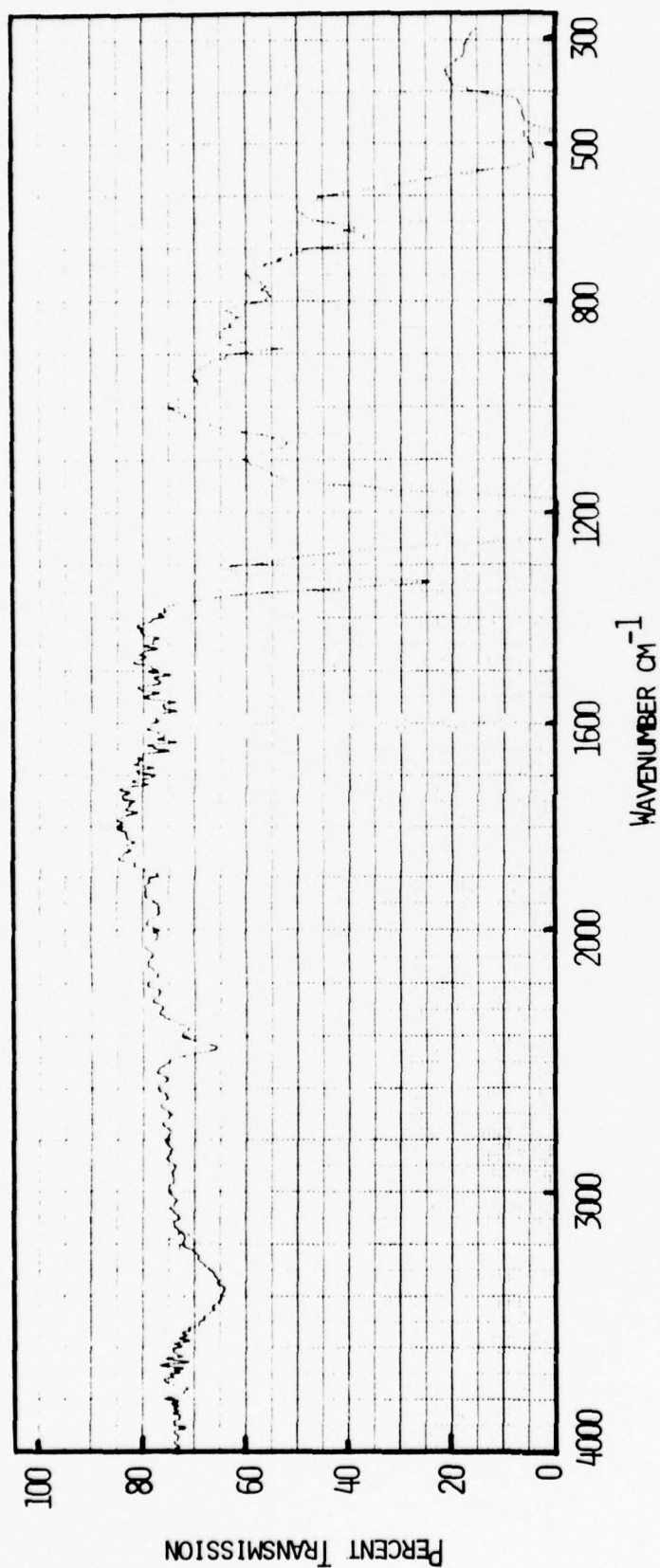


Fig. 14. Infrared spectrum of the electrolyte from cell P-41 after the test shown in Fig. 13.

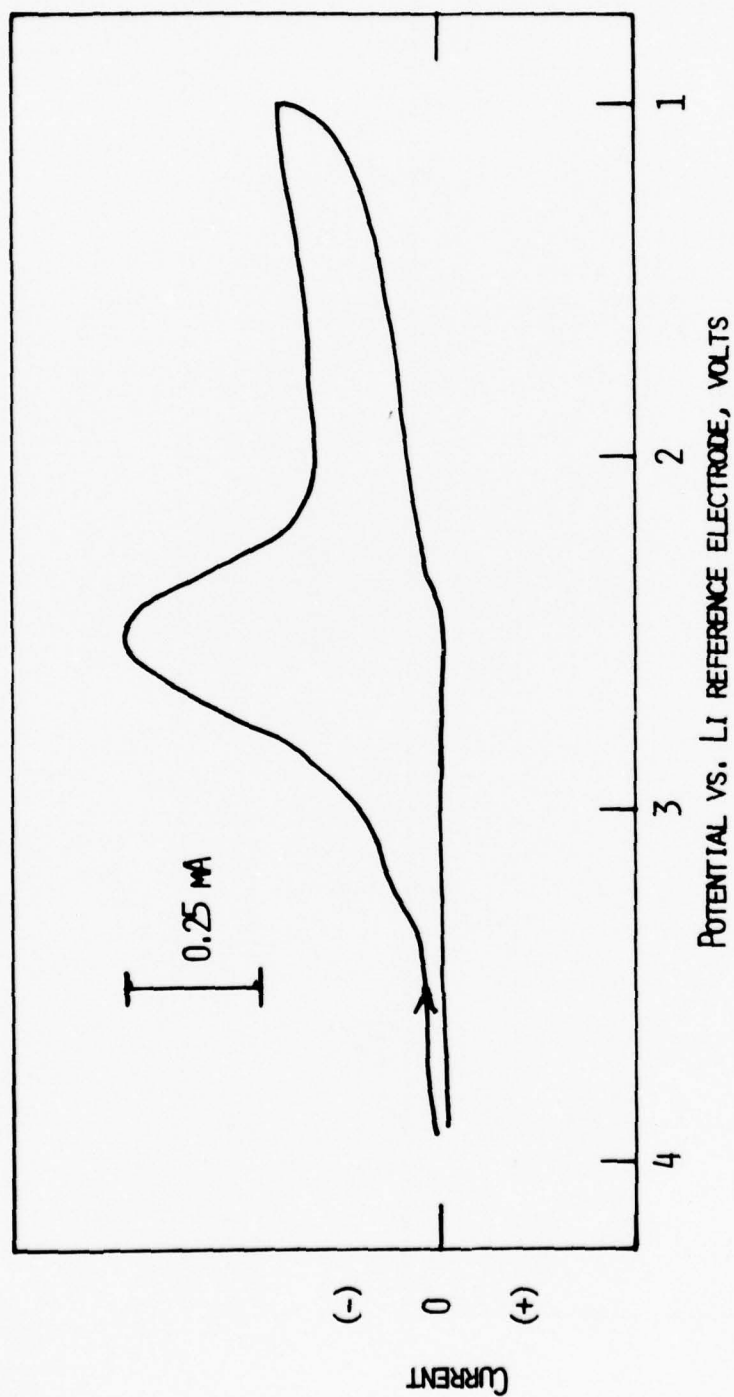


Fig. 15. Cyclic voltammogram of the electrolyte from cell P-41 after the forced over-discharge shown in Fig. 13. Sweep rate = 200 mV/sec. Cathodic scan first.

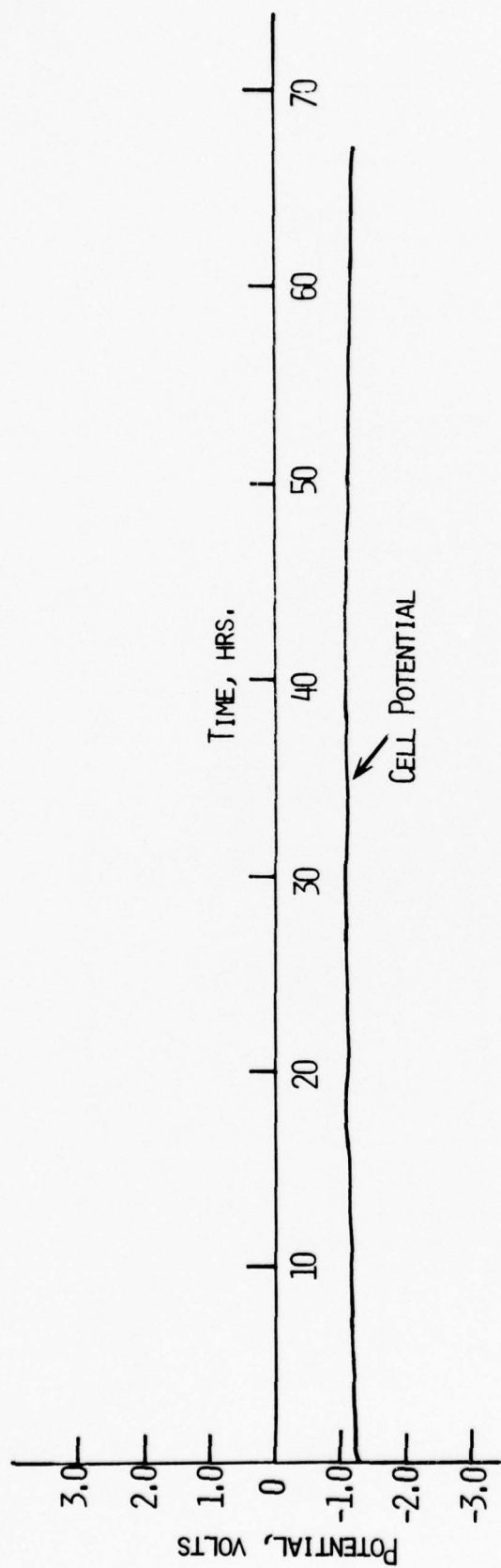


Fig. 16. Galvanostatic discharge curve for cell P-46. Current = 24 mA.

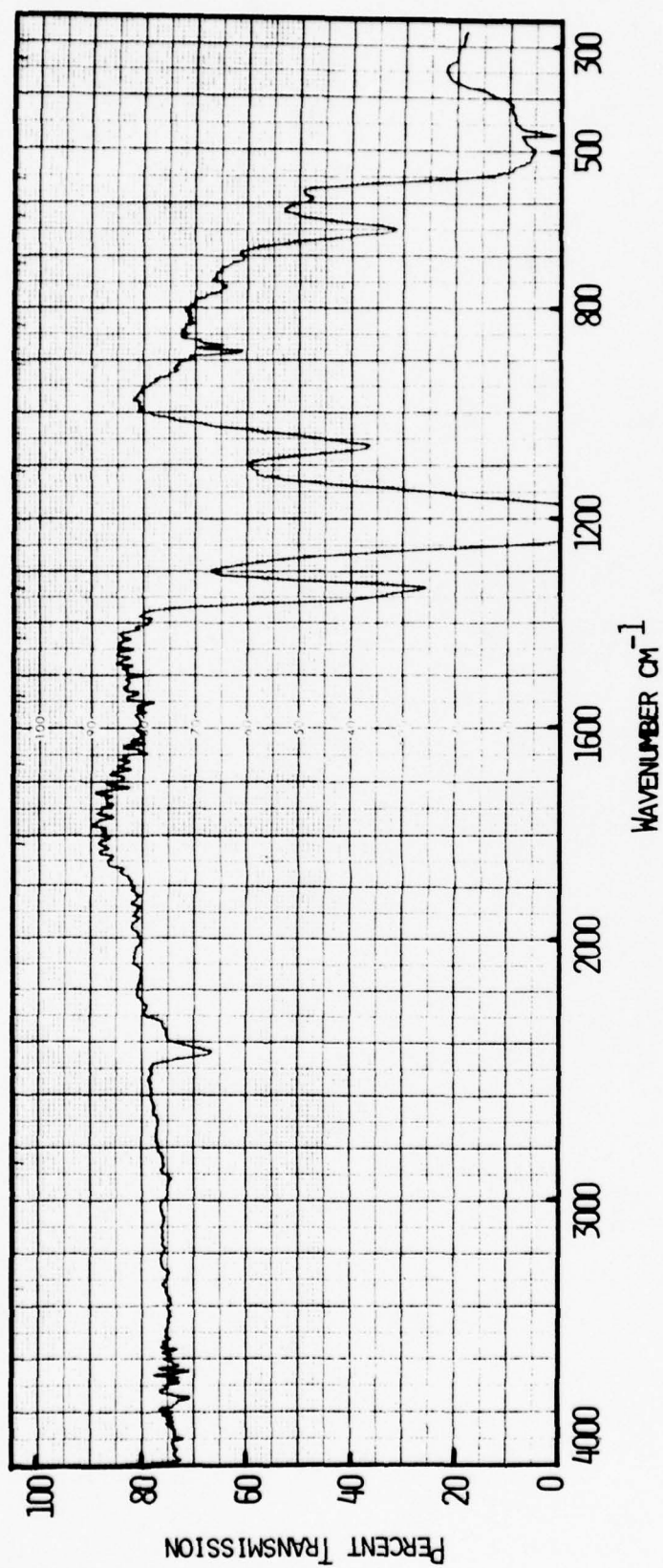
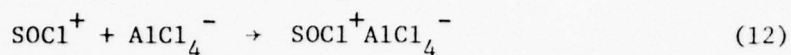
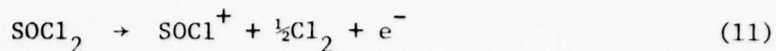


Fig. 17. Infrared spectrum of the electrolyte from cell P-46 after the test shown in Fig. 16.



Analytical data presented in the 2nd quarterly report indicated that the oxidation reactions 9 and 11 both occur at the anodic potentials exhibited by these cells. It is not surprising that in the present cell $\text{SOCl}^+\text{AlCl}_4^-$ is absent since the electrolyte does not apparently contain AlCl_4^- .

The cyclic voltammogram of the electrolyte from cell P-46 is shown in Fig. 18. The features of the voltammogram are identical to those found previously in the electrolyte from similarly tested cells containing $\text{SOCl}_2/\text{LiAlCl}_4$. The current peaks at $\sim 3.6\text{V}$ and $\sim 3.25\text{V}$ respectively are indicative of the presence of SCl_2 and Cl_2 .

4.2 Potential Role of SO_2Cl_2 in the Production of Explosive Chemicals

We have shown previously that SO_2Cl_2 is one of the oxidation products of $\text{SOCl}_2/\text{LiAlCl}_4$ solutions. It is produced in the cell under various oxidizing conditions. In an attempt to assess whether the sensitive chemicals causing explosions in anode limited cells are produced from oxidation reactions of SO_2Cl_2 , cell P-48 was tested with $\text{SO}_2\text{Cl}_2/1.8\text{M LiAlCl}_4$. This cell did not contain any Li on the anode. This was done with the intention that any possible quenching reactions of Li with the products could be eliminated. The discharge curves for cell P-48 is shown in Fig. 19. As in similar cells with $\text{SOCl}_2/\text{LiAlCl}_4$, the cell processes during discharge are regenerative so that no polarization of the cell voltage from the initial value is observed in the course of passing 3.25 Ah charge. The cell contained only a little more than 2 Ah of SO_2Cl_2 . The IR spectrum of the electrolyte after the test is shown in Fig. 20. The spectrum shows the presence of SO_2 (1335 cm^{-1}) and a small amount of the material exhibiting the absorption at 1070 cm^{-1} . All the other absorptions in the spectrum can be ascribed to SO_2Cl_2 . Cyclic voltammogram on the electrolyte showed that some Cl_2 is also present. The cell did not explode and handling of the electrolyte was hazard free.

5. Products from "Charged" Li/ SOCl_2 Cells

We have shown previously that the constant current "charging" of Li/ SOCl_2 cells leads to regenerative processes so that these cells can be "charged" indefinitely. Product analysis after the charge showed that a net accumulation of SO_2Cl_2 , SCl_2 , Cl_2 , SO_2 and the material with IR absorption at 1070 cm^{-1} occurs. The cell potentials during "charging" remain steady but their values depend on the state of discharge. Thus, in a partially discharged cell, the charging potentials were at $\sim 3.8\text{V}$ as opposed to $\sim 4.2\text{V}$ in fresh cells. In order to see if this was due to different types of regenerative processes, cell P-47 was partially discharged first and then "charged" and the products were analyzed

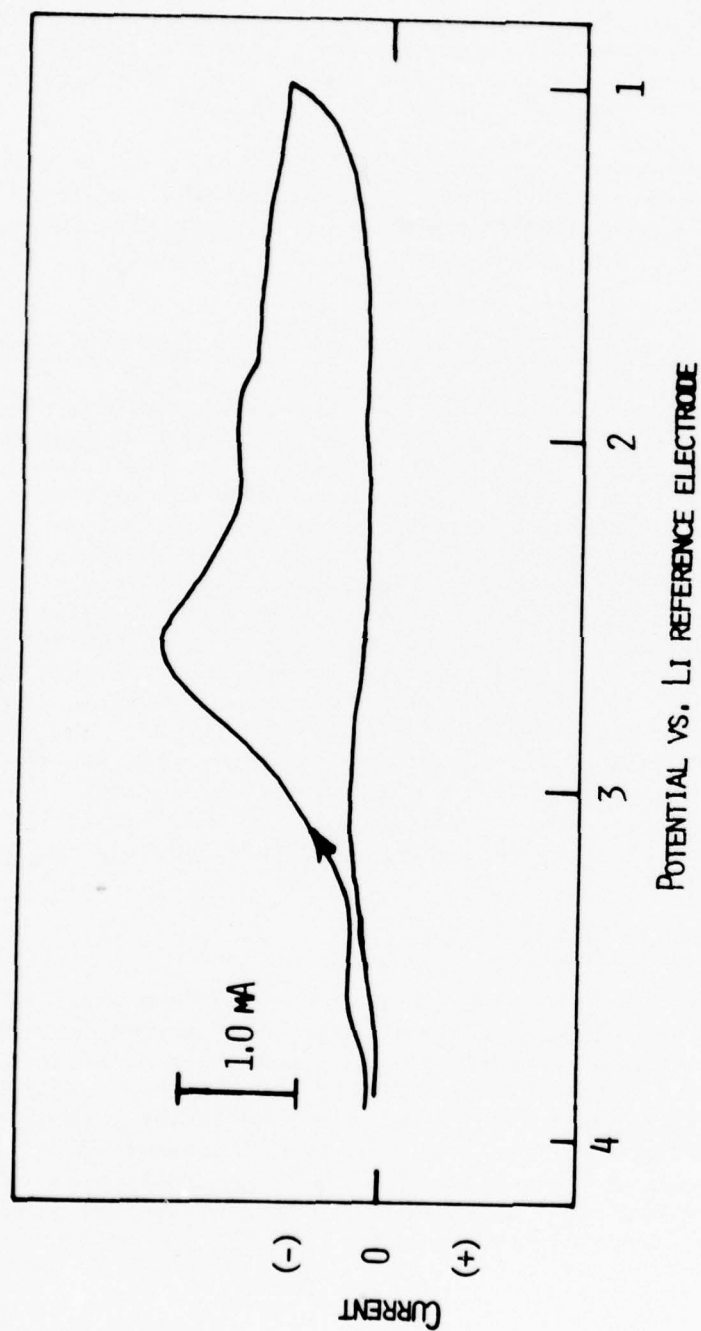


Fig. 18. Cyclic voltammogram of the electrolyte from cell P-46 after the discharge shown in Fig. 16. Sweep rate = 200 mV/sec. Cathodic scan first.

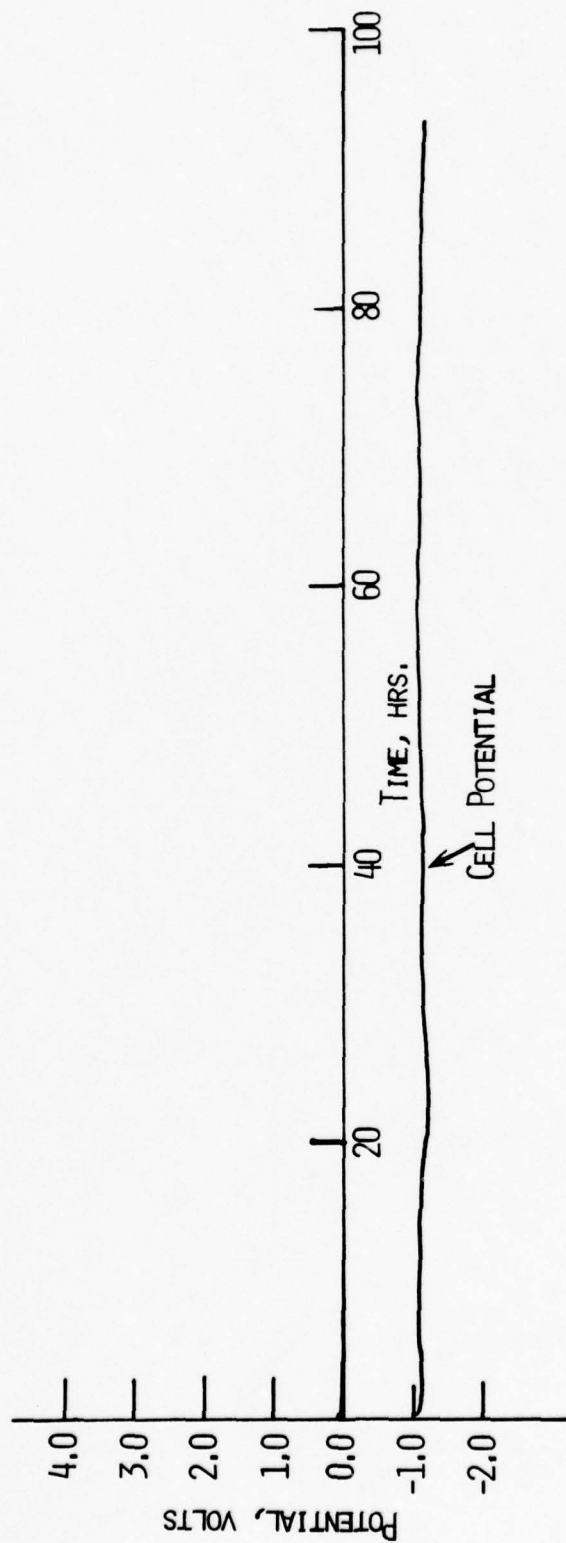


Fig. 19. Galvanostatic discharge curve for SO_2Cl_2 cell p-48. Current = 24 mA. The cell did not contain any Li.

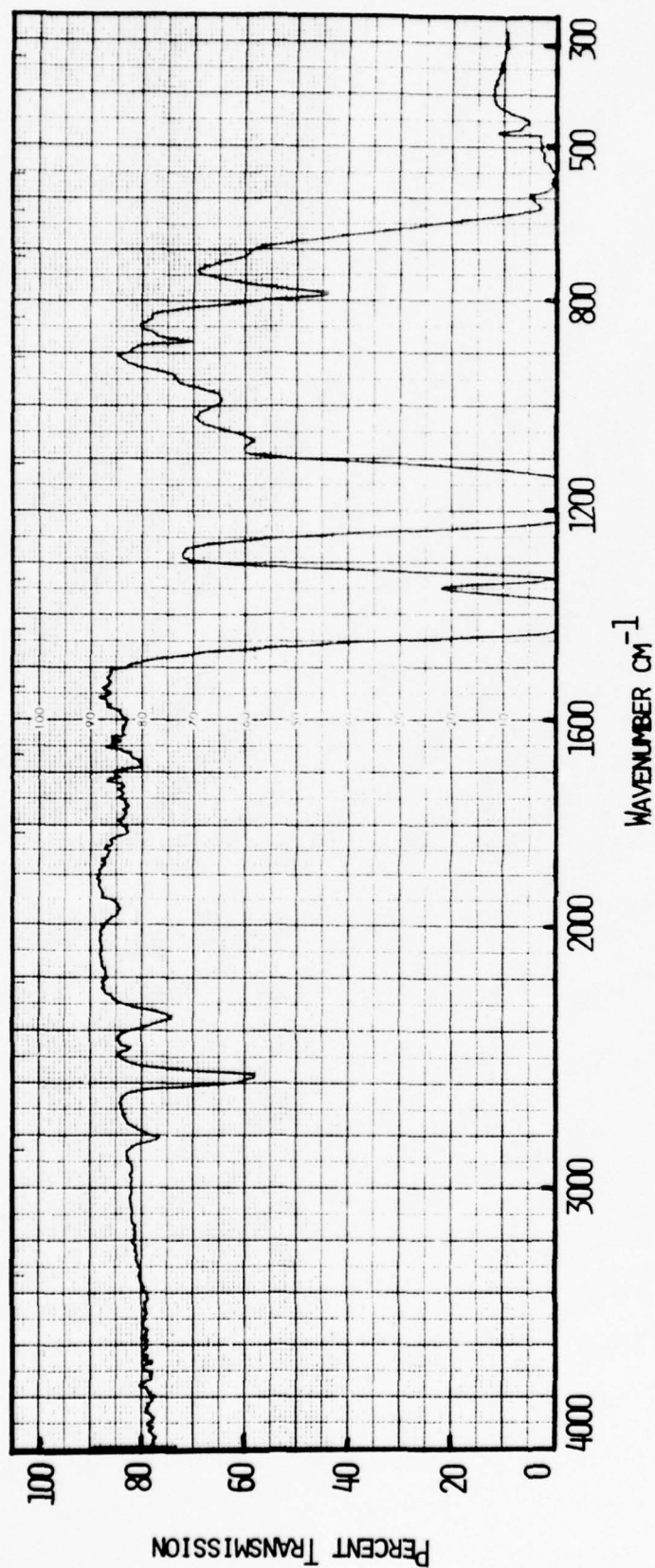


Fig. 20. Infrared spectrum of the electrolyte from cell P-46 after the test shown in Fig. 19.

by IR spectrometry and cyclic voltammetry. The discharge and "charge" curves are shown in Fig. 21. The initial discharge was for 0.61 Ah, about half the useful capacity of the cell. The cell was "charged" for 3.35 Ah. Note that the charging potentials remained steady at ~ 3.8 V as found previously. The IR spectrum and cyclic voltammogram on the electrolyte are shown in Figs. 22 and 23 respectively. The IR spectrum shows the presence of SO_2 and the material with IR absorption at 1070 cm^{-1} , but SO_2Cl_2 is not present. The cyclic voltammogram shows the Cl_2 reduction peak at ~ 3.25 V, but no SCl_2 is present. From mechanistic studies, we have shown that SO_2Cl_2 and SCl_2 are produced by a secondary oxidation reaction of the complex $\text{SOCl}^+\text{AlCl}_4^-$. It appears that this reaction does not occur during charging of partially discharged cells. This suggests that the regenerative process in this case involve a different set of reactions from those in fresh cells.

We have also investigated the nature of products on "charging" of fresh cells containing $\text{SOCl}_2/0.5\text{M LiAlCl}_4$. Normally the cells contain $\text{SOCl}_2/1.8\text{M LiAlCl}_4$. All the products found in cells with $\text{SOCl}_2/1.8\text{M LiAlCl}_4$ have been found here also.

In cell P-43 the nature of the products during "charging" was investigated with $\text{Li}_2\text{O}/\text{AlCl}_3$ based electrolyte. Here also the electrolyte had 1M Li^+ ion concentration. The construction parameters of the cell are shown in Table 1. The "charging" curve for the cell at 36 mA constant current is shown in Fig. 24. The potential profiles are identical to those found in cells with $\text{SOCl}_2/\text{LiAlCl}_4$. The IR spectrum and cyclic voltammogram of the electrolyte are shown respectively in Figs. 25 and 26. The data are identical to the electrolyte from "charged" cell containing $\text{SOCl}_2/\text{LiAlCl}_4$ showing that the overall processes are identical.

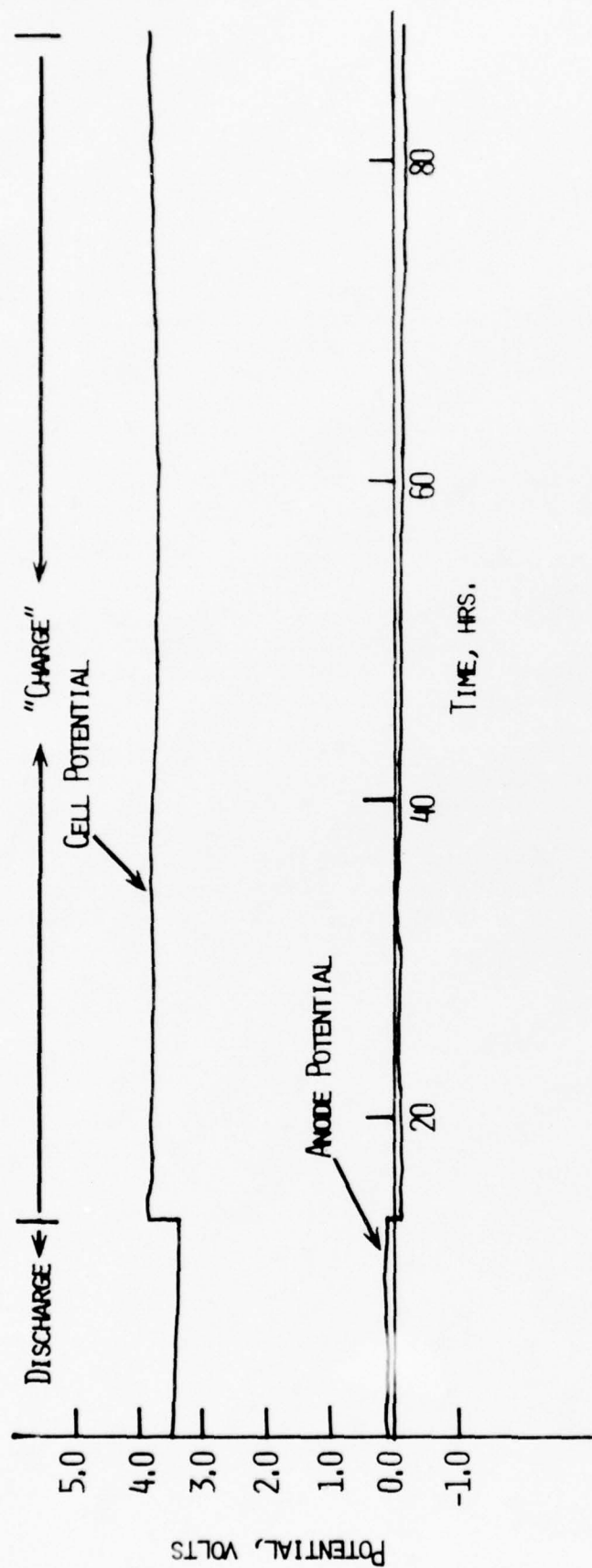


Fig. 21. Galvanostatic discharge and "charge" curves for cell P-47. Current = 36 mA.

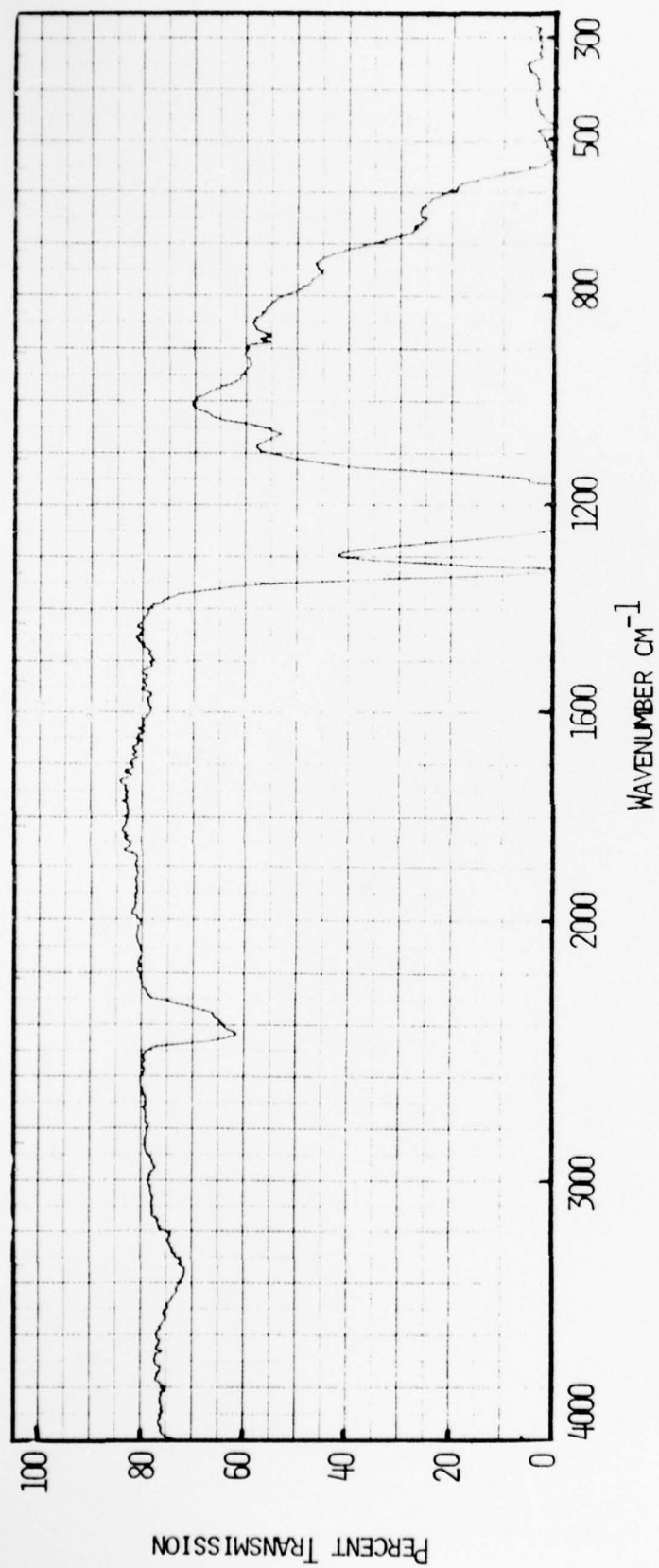


Fig. 22. Infrared spectrum of the electrolyte from cell P-47 after the test shown in Fig. 21.

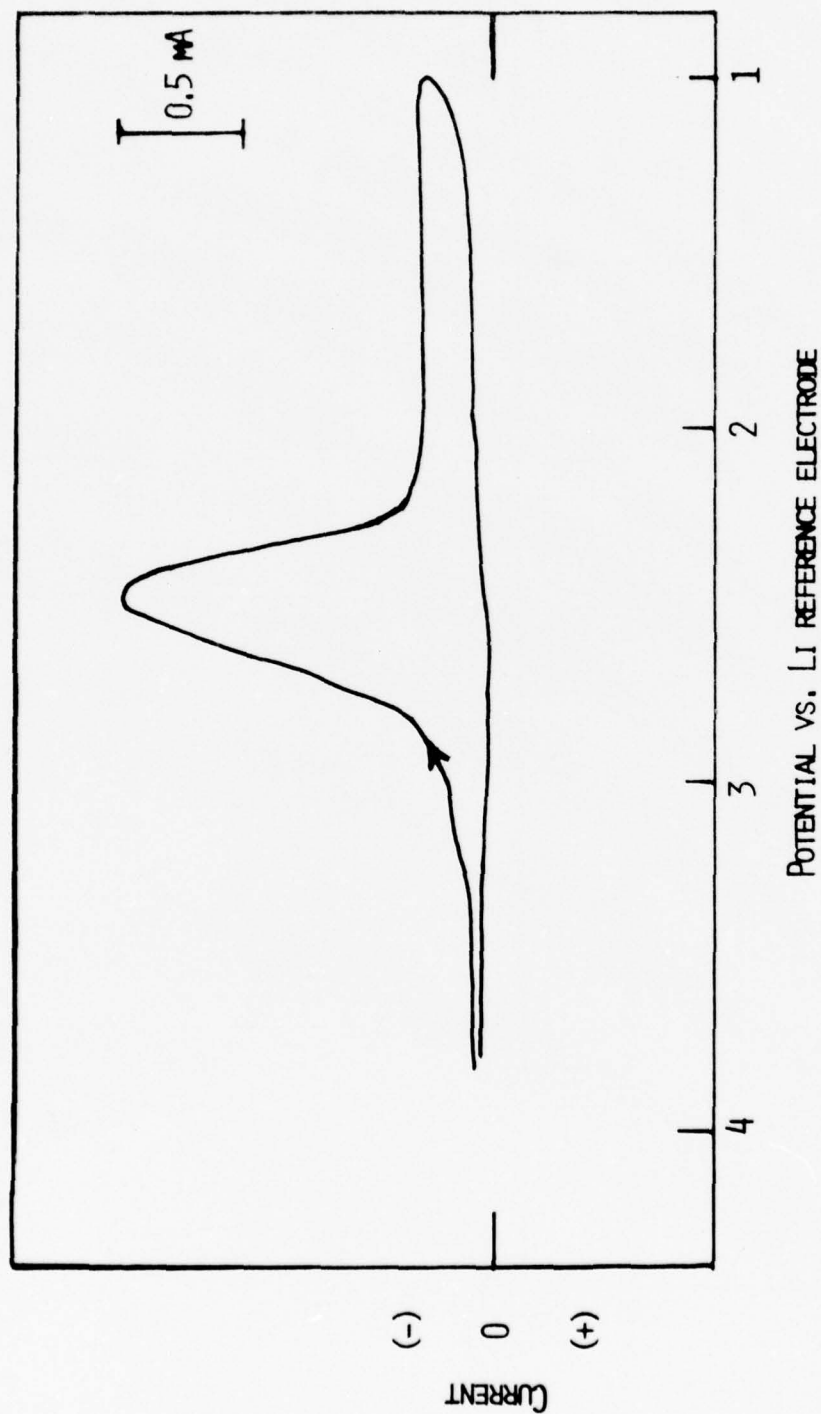


Fig. 23. Cyclic voltammogram of the electrolyte from cell P-47 after the tests shown in Fig. 21. Sweep rate = 200 mV/sec. Cathodic scan first.

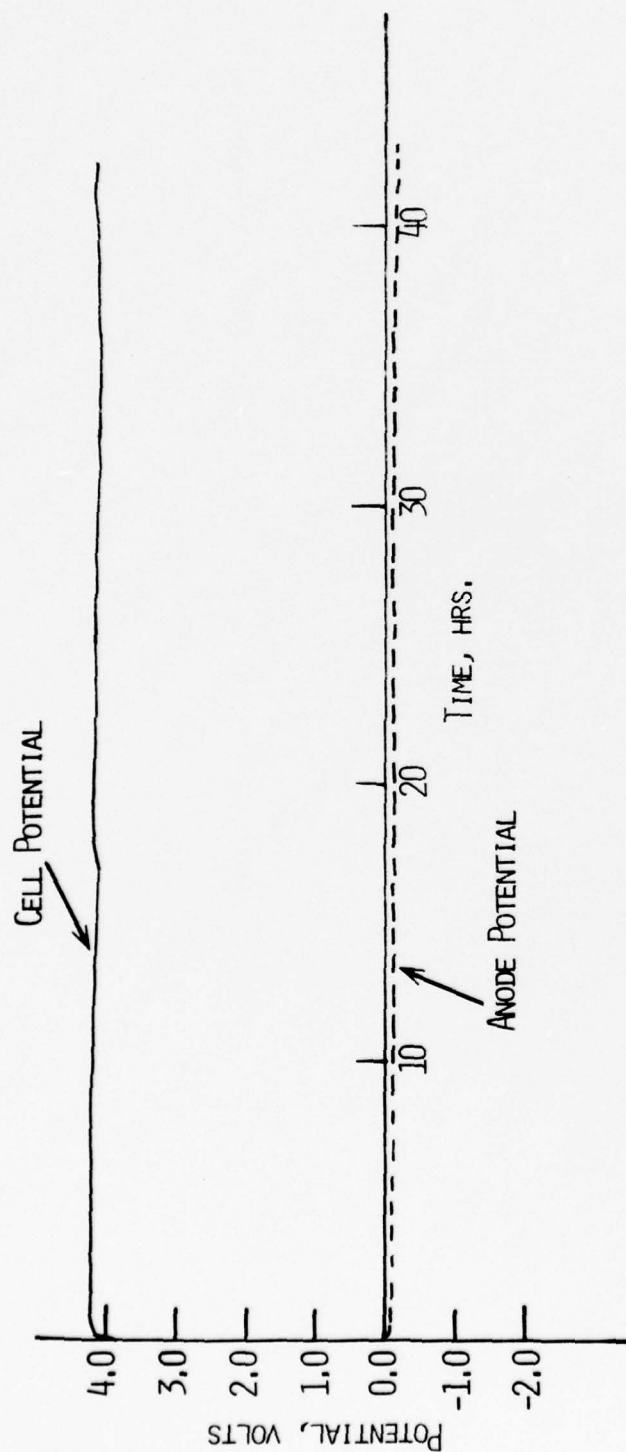


Fig. 24. Galvanostatic "charging" curve for cell P-43. Current = 36 mA.

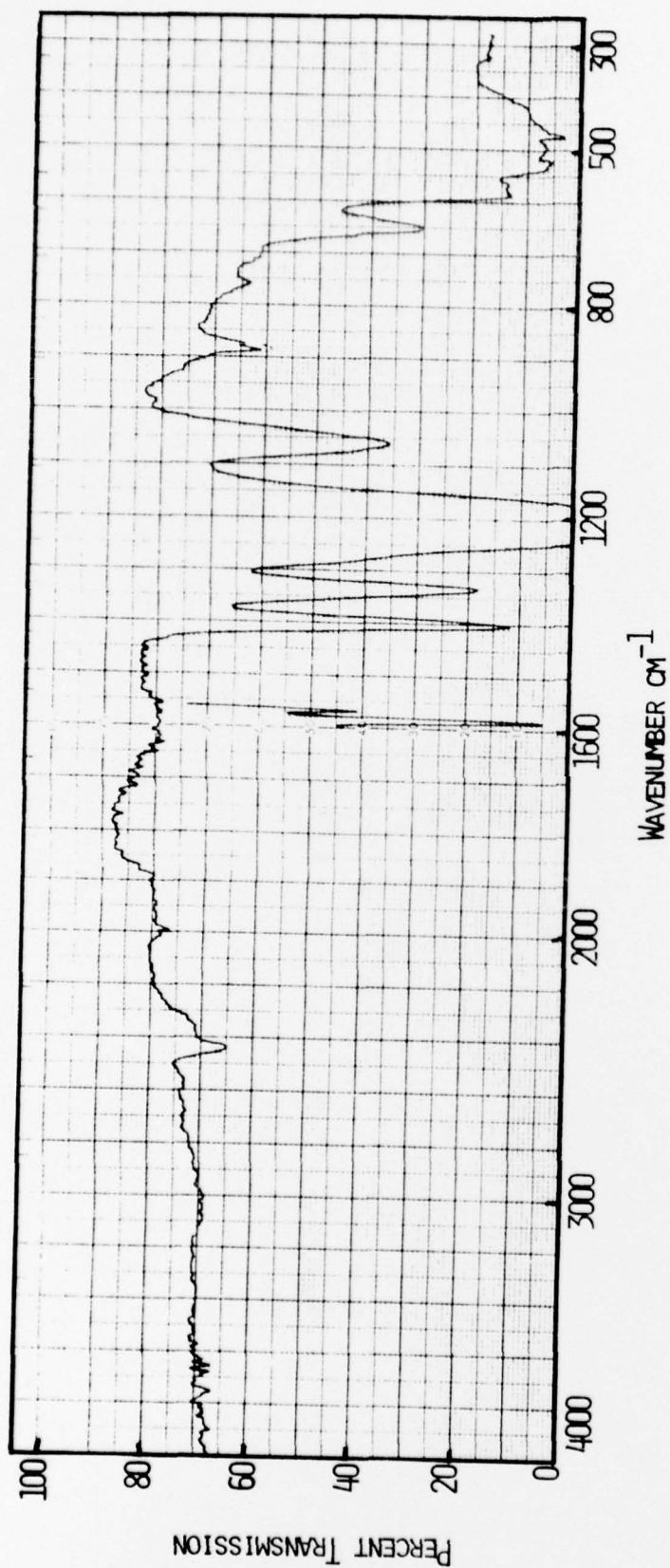


Fig. 25. Infrared spectrum of the electrolyte from cell P-43 after the test shown in Fig. 24.

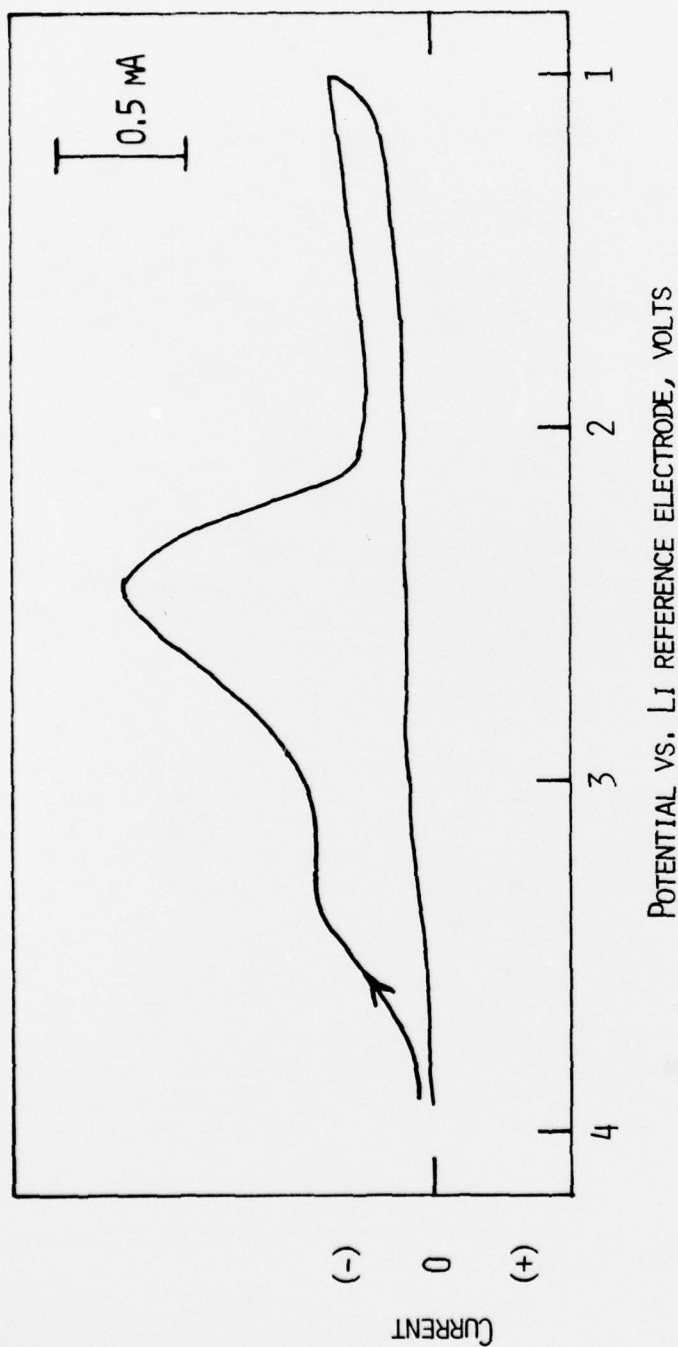


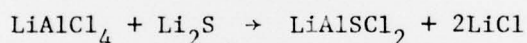
Fig. 26. Cyclic voltammogram of the electrolyte from cell P-43 after the "charging" shown in Fig. 24. Sweep rate = 200 mV/sec. Cathodic scan first.

III. SUPPORTING ELECTROLYTE BASED ON Li₂S/AlCl₃ FOR Li/SOCl₂ CELLS

In the previous section we have shown that the reaction of Li₂S with AlCl₃ in SOCl₂ produces LiAlSCl₂ or a mixture of LiAlSCl₂ and LiAlCl₄ depending upon the stoichiometry of the reactants.* A solution of LiAlSCl₂ in SOCl₂ can be obtained by treating AlCl₃ and Li₂S in a 1:1 molar ratio. When Li₂S and AlCl₃ are treated in a 1:2 molar ratio, the products are LiAlSCl₂ and LiAlCl₄. Both of these solutions were found to be good electrolytes having conductivities similar to that of SOCl₂/LiAlCl₄ solutions.

1. Conductivities of Li₂S/AlCl₃ Solutions in SOCl₂

The conductance data were obtained using a conductivity cell of the Jones and Bollinger type. The variation of specific conductances of 1M AlCl₃ solution in SOCl₂ as a function of the concentration of added Li₂S is shown in Fig. 27. The conductivity of the solution with 0.5M Li₂S is $16 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and the solution apparently contains 0.5M each of LiAlSCl₂ and LiAlCl₄. Up to this concentration of Li₂S there is no precipitate formed in solution with the incremental addition of Li₂S. With further addition of Li₂S a precipitate is formed which is due to LiCl formed according to the reaction



The conductance data were obtained with precipitate-free electrolytes. The conductance of the solution with 1M Li₂S is $\sim 13 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. When compared to the specific conductivity of $14 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ for 1M LiAlCl₄/SOCl₂ solutions, the Li₂S/AlCl₃ solutions should exhibit discharge performance similar to solutions with LiAlCl₄ salt. Preliminary data suggest that this would be possible.

2. Performance of Cells with Li₂S/AlCl₃ Based Electrolytes

Two cathode limited cells were tested. The construction parameters for these cells are given in Table 3. In cell P-52, the electrolyte was a mixture of LiAlSCl₂ and LiAlCl₄ obtained by stirring Li₂S (0.5M) and AlCl₃ (1M) in SOCl₂ so that the Li⁺ ion concentration was 1M. The OCV of the cell was 3.7V. It was

*As mentioned previously, it remains to be established whether SOCl₂ reacts with Li₂S in the presence of AlCl₃.

SPECIFIC CONDUCTANCE $\times 10^3$, $\text{OHM}^{-1}\text{CM}^{-1}$

Li_2S , mol/AlCl_3 (1M) IN SOCl_2

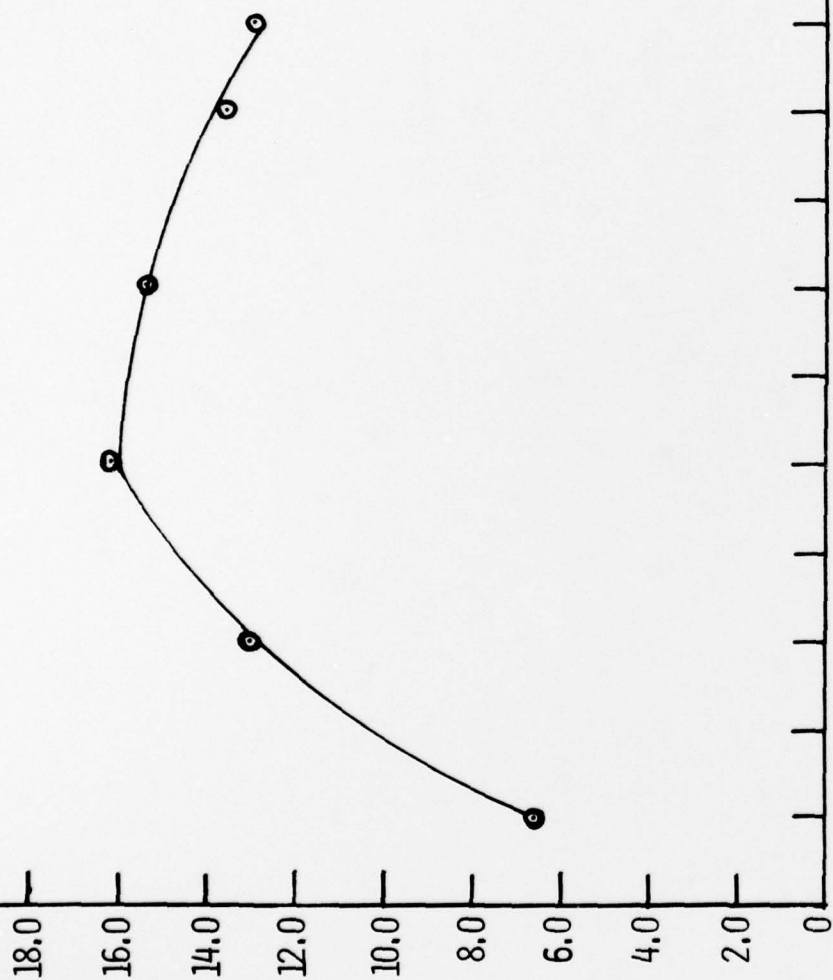


Fig. 27. Conductometric titration of AlCl_3 dissolved in SOCl_2 (1M) with Li_2S .

Table 3

Cell Parameters for Li/SOCl₂ Cells with Li₂S/AlCl₃ based Electrolytes

Cell No.	Cell Configuration	Carbon Electrode			Lithium Electrode		Electrolyte		
		Average Thickness (mm)	Total Area Facing Li (cm ²)	Approximate Amount of Carbon (mg)	Area (cm ²)	Amount (Ah)	[Li ⁺] (M)	Vol. (ml)	Discharge Current (mA)
51	Cathode Limited	0.55	36	340	36	2.01	1.0 ^a	4	36
52	Cathode Limited	0.52	36	330	36	2.01	1.0 ^b	4	36

^a1M LiAlCl₂.^b~0.5M LiAlCl₂ + ~0.5M LiAlCl₄.

discharged at 36 mA (1 mA/cm^2 of Li electrode area). The discharge curve is shown in Fig. 28. The cell yielded 1.0 Ah capacity to zero volt, corresponding to a cathode utilization of 3.07 Ah/g carbon. This utilization is virtually identical to that obtained from cells with $\text{SOCl}_2/\text{LiAlCl}_4$.

In cell P-51, the electrolyte was solution of LiAlSCl_2 (1M) in SOCl_2 , obtained by treating equimolar amounts of Li_2S and AlCl_3 in SOCl_2 and filtering off the precipitated LiCl . The OCV of the cell was also 3.7V and it was also discharged at 36 mA, Fig. 29. The cell capacity was 0.98 Ah, which corresponded to a cathode utilization of 2.93 Ah/g carbon.

These data suggest that $\text{Li}_2\text{S}/\text{AlCl}_3$ based electrolyte show promise as alternatives for LiAlCl_4 in Li/SOCl_2 cells. Further work is in progress.

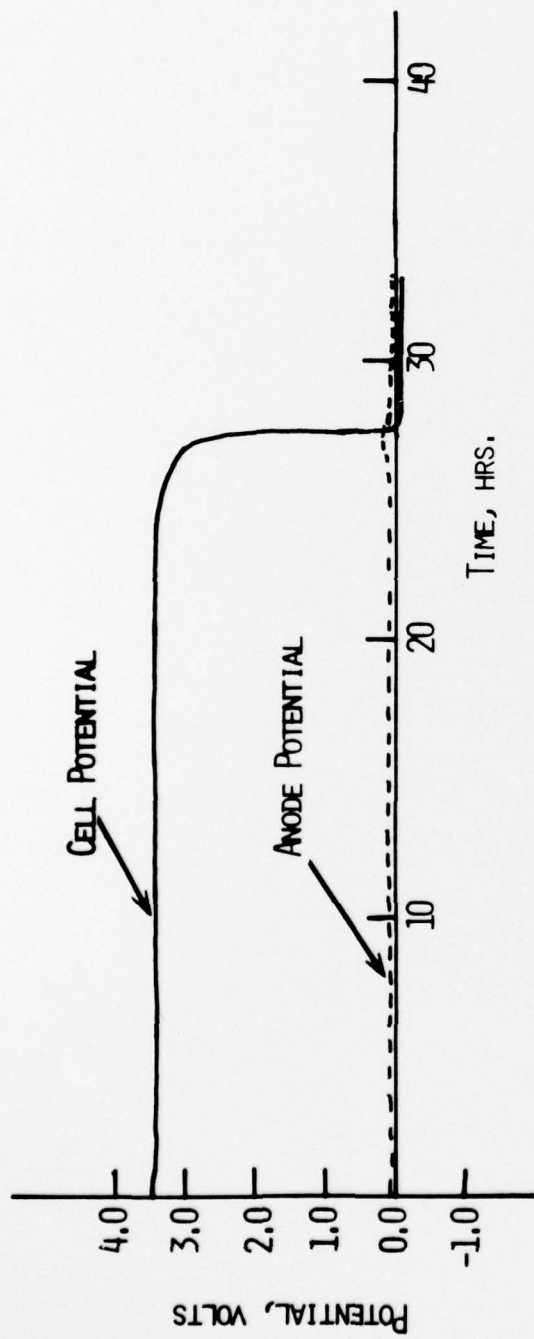


Fig. 28. Galvanostatic discharge curves for cell P-52. Current = 36 mA.

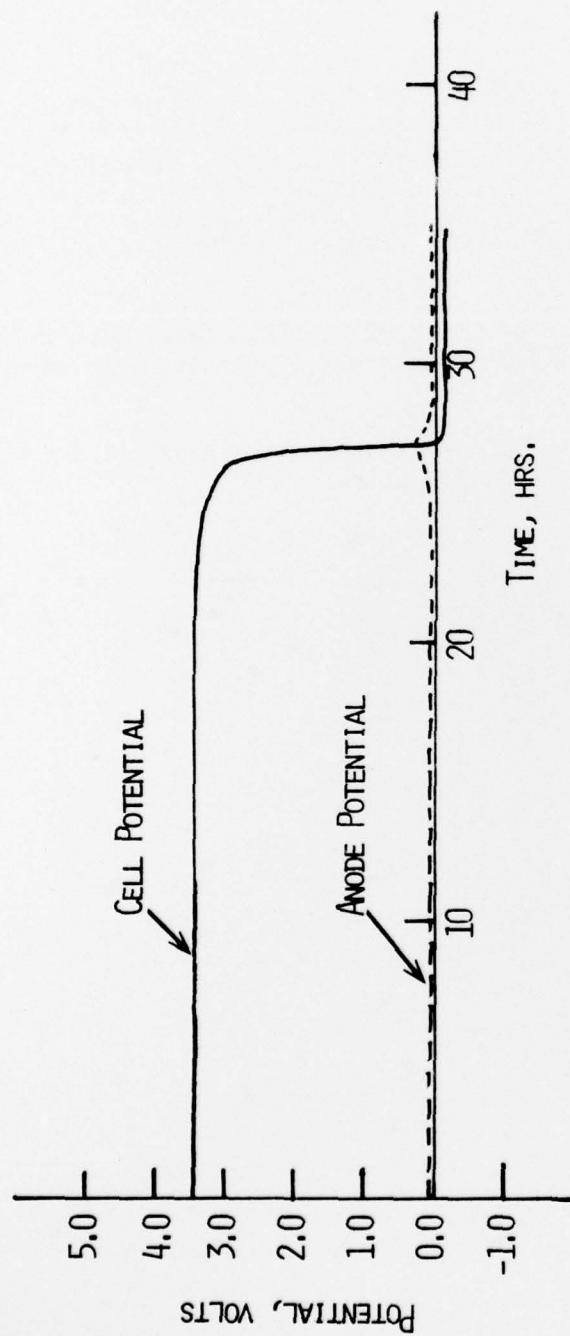


Fig. 29. Galvanostatic discharge curves for cell P-51. Current = 36 mA.

IV. SUMMARY AND FUTURE WORK

Infrared spectral data of electrolyte from forced overdischarged cathode limited cells indicated that LiAlSCl_2 and probably LiAlS_2 are produced. These compounds have also been identified in cathode limited cells after resistive load overdischarge. Isolation experiments suggested that these compounds are formed from the reaction of Li_2S with LiAlCl_4 . We have also found that the lithium thioaluminum compounds can be prepared from the reaction between Li_2S and AlCl_3 .

Analysis of products from cells utilizing $\text{Li}_2\text{O}/\text{AlCl}_3$ based electrolyte did not show any significantly different products after overdischarge or constant current "charge".

Preliminary studies showed that $\text{Li}_2\text{S}/\text{AlCl}_3$ based electrolytes may be useful as alternatives to LiAlCl_4 in Li/SOCl_2 batteries.

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